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Solid state synthesis and thermal stability of HAP and HAP – β-TCP composite ceramic powders

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Powders of pure β-tricalcium phosphate (β-TCP), hydroxyapatite (HAP) and a biphasic composite mixture of HAP + β-TCP were prepared by solid state reaction between two commercially available calcium-based precursors namely, tricalcium phosphate (TCP) and calcium hydroxide ($Ca(OH)_2$). These reactants mixed in the molar ratios ranging from 3:0 to 3:4 (designated T_0 to T_4) in deionized water, milled and slip-cast into discs were heat treated in the temperature range of 600 °C to 1250 °C. The products formed were characterized by X-ray diffraction (XRD) and i.r. spectroscopic techniques for identification of phases formed and functional groups present in them. While tricalcium phosphate and calcium hydroxide taken in the molar ratio of 3:2 and 3:3 resulted in pure HAP when heat treated at 1000 °C for 8 h, the 3:1 and 3:1.5 molar ratio compositions resulted in a biphasic mixture of HAP + β-TCP for similar heat treatments. Heat treatment of 3:4 molar ratio composition of tricalcium phosphate and calcium hydroxide at 1000 °C yielded HAP with free CaO as the secondary phase. Products of heat treatment at higher temperatures (1150 and 1250 °C) for even shorter duration (2 h) while not differing from the products obtained from T_0 and T_2 cases at 1000 °C (pure β-TCP and pure HAP), change in the case of T_1, $T_{1.5}$, T_3 and T_4 to products with lesser percentages of HAP containing β-TCP (in the case of T_1 and $T_{1.5}$) or CaO (in the case of T_3 and T_4) as the secondary phase.

1. Introduction

Calcium phosphates of varied composition are present to a large extent in our teeth and bone tissues. Hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) is the major inorganic constituent amounting to 69% by weight in bones. Other phosphates present in minor amounts in bones include calcium pyrophosphate (CPP; $Ca_2P_2O_7$), tricalcium phosphate (TCP; $Ca_3(PO_4)_2$) and tetracalcium phosphate (TTCP; $Ca_4P_2O_9$) [1]. The calcium phosphate minerals, being primary constituents of the hard tissues, have superior biocompatibility and a better capability of directly integrating to bone tissues by their resorption (e.g. β-TCP) or by allowing the intergrowth of new bones into their porous structure (HAP). They have therefore emerged, during the last two decades, as important bone and teeth implant materials. Hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP) are particularly attractive materials for hard tissue implants in oral and plastic surgery or for use as bone (powder) fillers for filling up gaps (e.g. during resetting of complicated bone fractures with considerable loss of bone material or in case of large voids formed due to the removal of large tumours in young patients etc.) [2–6]. Hence, there is a great need to produce these calcium phosphates for clinical uses in appropriate forms.

Methods have been proposed and developed for preparation of HAP possessing various Ca:P stoichiometries and β-TCP from aqueous solution by precipitation from soluble calcium/phosphorus salts and phosphoric acid [7–13]. Apatite ceramics have also been produced by slip-casting slurries containing mixtures of tricalcium phosphate and calcium hydroxide or calcium carbonate in a molar ratio of 3:1 in plaster moulds, followed by sintering [14–16]. However, little evidence is available about the solid state reaction of two intimately mixed calcium-based reactants by heat treatment at high temperatures to obtain stoichiometric HAP or a HAP + β-TCP biphasic composite powders.

The present study is aimed at producing powders of β-TCP, HAP and mixtures of HAP and β-TCP from mixtures of commercially available calcium phosphate (tribasic) and calcium hydroxide ($Ca(OH)_2$) powders.

2. Experimental procedure

2.1. Sample preparation

The starting materials used were calcium phosphate (tribasic) (M/S Robert Johnson, India) and calcium hydroxide (laboratory reagent, M/S Ranbaxy, India). The as-received powders were characterized for their

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phase contents by X-ray (CuK_α) diffraction (XRD) (model PM9002 diffractometer, M/S Philips, Holland) and for presence of various functional groups e.g. PO_4^{3-}, OH^- etc. by i.r. spectroscopic techniques using an i.r. spectrophotometer (model 682, M/S Perkin-Elmer). As-received commercial calcium phosphate (tribasic) (herein after denoted as TCP) and calcium hydroxide powders in various proportions ranging from 3 : 0 to 3 : 4 molar ratios respectively (such samples are designated as, T_x, where $0 < x < 4$, depending upon the number of moles of $Ca(OH)_2$ added to 3 moles of TCP) were dispersed in deionised water to a solid loading of about 50 wt% as presented in Table I. The slips having pH ≈ 12 were milled with alumina balls in polythene jars for 12 h (for disintegrating the agglomerates and aiding the homogeneous mixing of the reactants). The milled slips were cast into plaster of Paris moulds in the form of discs (18 mm diameter × 10 mm thick). Cast bodies released after 30 minutes from the moulds were dried at the laboratory temperature (30 °C) for 24 h and thereafter at 80 °C for 12 h.

2.2. Thermal treatment and characterization

The slip-cast and dried bodies of T_0, T_1, T_2 and T_3 powder mixtures were reacted in separate experiments at 600, 700, 800 and 1000 °C for 8 h and also at 1150 and 1250 °C, for only 2 h in air (to avoid any chance of decomposition of products at these higher temperatures) in a silicon carbide furnace. $T_{1.5}$ and T_4 samples were also heat treated only at 1000 °C for 8 h and also at 1150 and 1250 °C for 2 h. Most of the heat-treated discs could be hand crushed to powders easily and hence the products were considered to be in powder form. The heat-treated products were characterized for phase contents by XRD and for the functional groups present by i.r. techniques.

The morphology of powder products was observed in a scanning electron microscope (SEM) (model JSM-35, M/S Jeol, Japan). The particle size distribution of the bulk products were also determined using sedimentation analysis (Sedigraph, Model 5100, M/S Micromeritics, USA).

3. Results and discussion

3.1. Formation of HAP and HAP + TCP composite powders by heat treatments in the temperature range 600–1000 °C/8 h and 1150–1250 °C/2h

3.1.1. XRD spectral studies

The different compositions of TCP and TCP + $Ca(OH)_2$ precursor mixtures used and details of the heat treatments given are presented in Table I. The typical XRD patterns of starting TCP material (T_0)

TABLE I Different crystallographic phases analysed by X-ray diffraction method for TCP + $Ca(OH)_2$ combinations after heat treatments at various temperature/time cycles

Thermal treatment Temperature/time (°C/h)	Heat treated products evolved from β-TCP and $Ca(OH)_2$ mixtures[a]					
	3 : 0 (T_0)	3 : 1 (T_1)	3 : 1.5 ($T_{1.5}$)	3 : 2 (T_2)	3 : 3 (T_3)	3 : 4 (T_4)
80/12	HAP DCP DCPD	HAP DCP DCPD		HAP DCP DCPD CH	HAP DCP DCPD CH	
600/8	HAP βTCP βCPP	HAP βTCP βCPP DCPD		HAP βCPP DCPD CaO	HAP βTCP βCPP DCPD CH	
700/8	βTCP HAP βCPP	HAP βTCP βCPP		HAP βTCP βCPP	HAP βTCP βCPP CaO	
800/8	βTCP(93) HAP(7)	HAP(50) βTCP(50)		HAP(90) βTCP(6) CaO(4)	HAP(94) βTCP(6)	
1000/8	βTCP (100)	HAP(54) βTCP(46)	HAP(84) βTCP(16)	HAP (100)	HAP (100)	HAP(70) CaO(30)
1150/2	βTCP (100)	HAP(54) βTCP(46)	–	HAP (100)	HAP (100)	–
1250/2	βTCP (100)	HAP(49) βTCP(26) αTCP(25)	HAP(74) βTCP(26)	HAP (100)	HAP(90) CaO(10)	–

[a] Starting composition are presented in molar ratios (TCP: $Ca(OH)_2$) as designated below.

Crystallographic phases analysed: HAP = $Ca_{10}(PO_4)_6(OH)_2$, DCP = $CaHPO_4$, DCPD = $CaHPO_4 \cdot 2H_2O$, CH = $Ca(OH)_2$, βTCP = β–$Ca_3(PO_4)_2$, βCPP = β–$Ca_2P_2O_7$, αTCP = α–$Ca_3(PO_4)_2$.

heat treated at various temperatures (80 °C/12 h, 600 °C/8 h, 700 °C/8 h and 1000 °C/8 h) are presented in Fig. 1a–d. T_0 at 80 °C/12 h shows broad peaks corresponding to hydroxyapatite (HAP) present as agglomerated microcrystallites as well as peaks due to dicalcium phosphate ($CaHPO_4$, DCP) and dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, DCPD/brushite) present in minor quantities (Fig. 1a). The broad peaks of HAP as well as the presence of the latter two phases are also indicative of the existence of a certain quantity of calcium-deficient HAP ($Ca_9(HPO_4)(PO_4)_5OH$) cited by earlier authors [9, 13, 17]. On heat treatment at 600 °C, the XRD peaks corresponding to HAP remained unchanged while those due to DCP and DCPD disappeared to be replaced by those of decomposition products namely β-TCP (β-$Ca_3(PO_4)_2$) and β-calcium pyrophosphate ($Ca_2P_2O_7$, CPP) as shown in Fig. 1b. Beyond 600 °C the HAP structure starts slowly transforming to β-TCP (Fig. 1c) and at 1000 °C complete transformation to pure β-TCP [12, 17–19] phase occurs as shown in Fig. 1d. These changes are also shown in Table I under the T_0 column. The proportions of various phases present in well-crystallized forms resulting from heat treatment beyond 700 °C were calculated from the relative intensities of the strongest XRD peaks of the respective phases (e.g. 31.8° of 2θ for HAP and 31.0° of 2θ for β-TCP). These are shown in figures by the side of each phase in Table I. The results indicate that microcrystalline agglomerates of HAP and calcium-deficient HAP transform to crystalline β-TCP [9, 13, 18] in the temperature range 600–1000 °C.

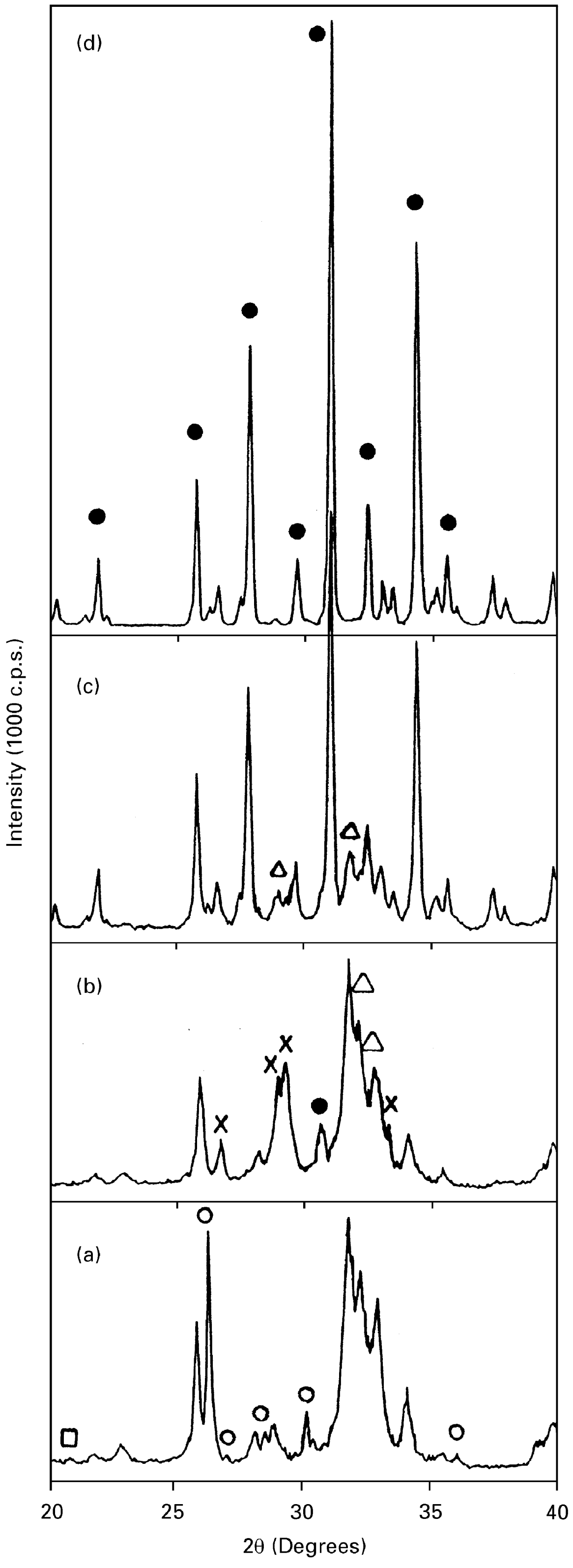


Figure 1 XRD spectra of starting TCP powder (a) 80 °C/12 h; (b) 600 °C/8 h; (c) 700 °C/8 h; (d) 1000 °C/8 h. (○) $CaHPO_4$, (□) $CaHPO_4 \cdot 2H_2O$, (×) $Ca_2P_2O_7$, (△) HAP, (●) β-TCP.

Although the starting composition of T_0 powder was not exactly known, its final composition on heating to 1000 °C was revealed by XRD to be that of β-TCP with a Ca/P ratio of 1.5. Hence T_0 was considered as a precursor with an average Ca/P ratio of 1.5 for all further studies. Mixtures of T_0 and $Ca(OH)_2$ in various proportions e.g. 3 : 1, 3 : 1.5, 3 : 2, 3 : 3, 3 : 4 etc. (designated as T_1, $T_{1.5}$, T_2, T_3 and T_4, respectively) were subjected to the same heat-treatment schedules as was done for T_0. The product phases obtained at various temperatures are set out in Table I. Their XRD spectra are presented in Figs 2 and 3.

The heat treatment of T_1 at various temperatures progressively alters the ratio of HAP to β-TCP in the product whose evolution is shown in Fig. 2a–d. In contrast with the T_0 case, wherein structural changes start occuring at $\approx$ 600 °C, when $Ca(OH)_2$ is added to the starting TCP to achieve a starting Ca/P ratio 1.67, the chemical and structural changes taking place below 700 °C are negligibly small and very sluggish. The well-crystallized phases begin to appear only above 700 °C and eventually on heat treatment at 1000 °C/8 h a HAP–β-TCP mixture in the ratio 54 : 46 (as derived from the intensities of most intense XRD peaks of the respective phases HAP and β-TCP) is obtained. The Ca/P ratio of this final product mixture calculated following the method of Ishikawa *et al.* [12] is 1.59, as against 1.67 based on starting mixtures overall composition.

Typical XRD spectra of the products of other starting powder mixtures $T_{1.5}$ (Ca/P ratio 1.75), T_2 (Ca/P ratio 1.83), T_3 (Ca/P ratio 2.0) and T_4 (Ca/P ratio 2.17) after heat treatment at 1000 °C/8 h are presented in Fig. 3a–c. Thus while HAP–β-TCP mixture in the ratio of 84 : 16 (Ca/P ratio 1.64) was obtained from $T_{1.5}$, 100% HAP (Ca/P ratio 1.67) was obtained for both T_2 and T_3 cases. However, T_4 yields a mixture of 70% HAP and 30% CaO (Ca/P ratio 1.738 for the total HAP + CaO mixture). CaO is identified in the

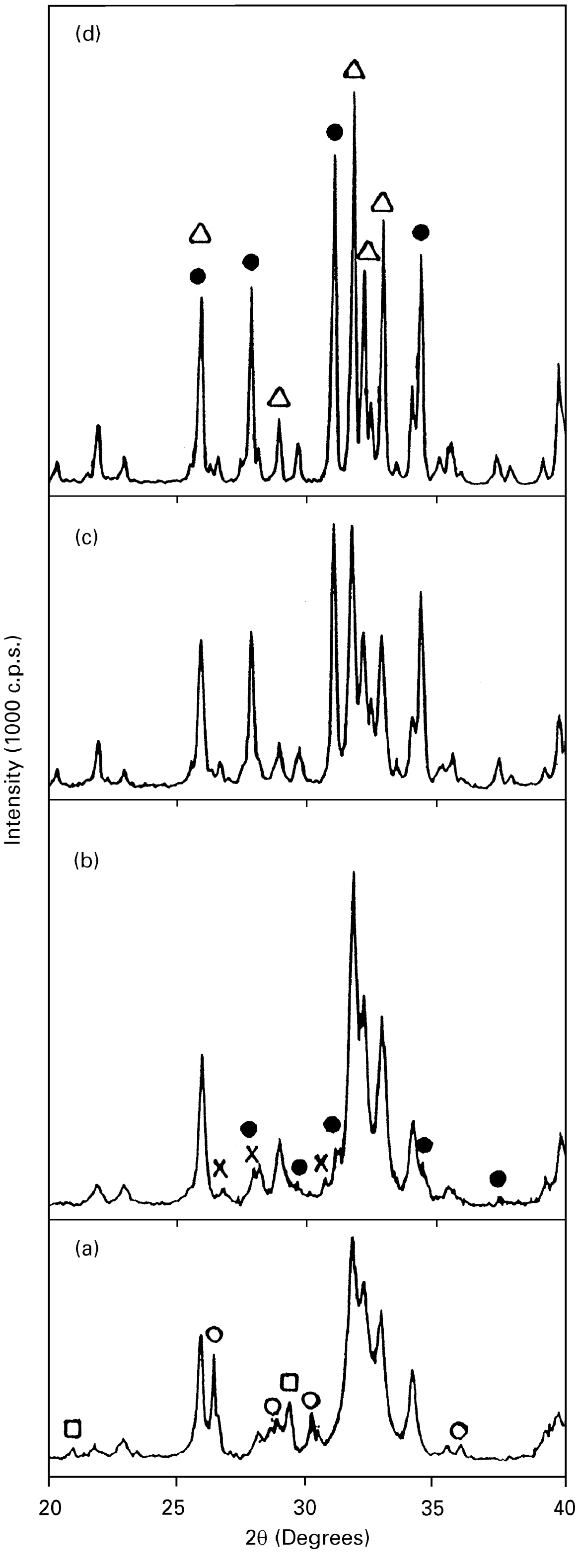


Figure 2 XRD spectra of TCP + $Ca(OH)_2$ mixture in the molar ratio of 3 : 1 (a) 80 °C/12 h; (b) 700 °C/8 h; (c) 800 °C/8 h; (d) 1000 °C/8 h. (○) $CaHPO_4$, (□) $CaHPO_4 \cdot 2H_2O$, (×) $Ca_2P_2O_7$, (●) β-TCP, (△) HAP.

XRD at 37.4° of 2θ. This study indicates that the most significant and stable products are obtained at 1000 °C/8 h, having an overall Ca/P ratio of close to 1.67 irrespective of the starting mixture composition for cases of T_1–T_3. Our observations are in accordance with those reported by Osaka *et al.* [9] for the case of precipitation reaction between calcium

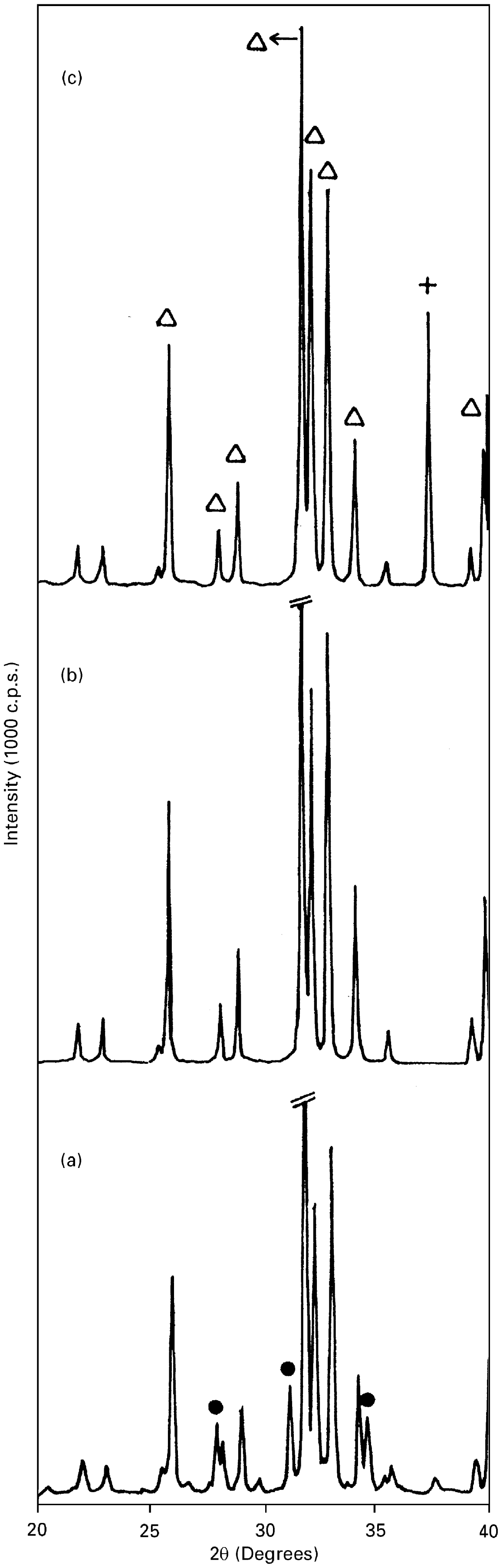


Figure 3 XRD spectra of TCP + $Ca(OH)_2$ mixture in the molar ratio of (a) 3 : 1.5; (b) 3 : 2 and 3 : 3; (c) 3 : 4 heat treated to 1000 °C for 8 h. (●) β-TCP, (△) HAP, (+) CaO.

hydroxide and orthophosphoric acid over a wide range of Ca/P starting mixture ratios (in order to obtain HAP–β-TCP mixtures, pure HAP and HAP + CaO mixtures) depending on the temperature of reaction. From the point of view of densification and sintering of HAP as well as the final end use, the product from T_4 is unsuitable since it contains CaO in appreciable quantities [11]. Hence, the starting compositions of T_0 to T_3 yield useful phases of products such as β-TCP, HAP + β-TCP and pure HAP on heat treatment to 1000 °C/8 h.

Heat treatments at temperatures higher than 1000 °C for shorter times (e.g. 2 h to avoid decomposition of products beyond 1000 °C) resulted in the retention of β-TCP formed from T_0 even at 1250 °C while a decrease in the quantity of HAP accompanied by a concomitant increase in the quantity of β-TCP formed was noted in the case of T_1 and $T_{1.5}$ starting compositions (see Table I). In the case of T_1 which contains appreciable amounts of β-TCP in the product partial conversion of β-TCP and HAP to α-TCP is noted. However, in the case of $T_{1.5}$ the product contains much less of β-TCP to undergo this conversion and no detectable α-TCP was seen in XRD. T_2 retained 100% pure HAP even on 1250 °C/2 h treatment while in the case of T_3 there was a slight decomposition of pure HAP to a mixture of 90% HAP + 10% CaO. It was seen already that T_4 yields a mixture of 70% HAP 30% CaO even at 1000 °C/8 h. Typical XRD spectra of the phases formed at 1250 °C are presented in Fig. 4a–c. These observations are again similar to those of Osaka *et al.* [9]. These high temperature heat-treatment studies further confirm that 1000 °C/8 h is the optimal temperature–time schedule for obtaining pure β-TCP, pure HAP and HAP–β-TCP mixtures from solid state reaction of commercial TCP and $Ca(OH)_2$.

3.1.2. Infrared spectral studies on the products

All the product samples were subjected to infrared spectral characterization studies and the results are supportive and complementary to the XRD results described in the previous section. Fig. 5a–f presents the i.r. spectra of T_0 and products of heat treatment of T_0, T_1, $T_{1.5}$, T_2, T_3 and T_4 at 1000 °C/8 h. Infrared spectra of products of T_1, T_2, and T_3 obtained at 1250 °C/2 h are shown in Fig. 6a–c. The i.r. spectra of various phases were assigned (from literature) as follows: PO_4^{3-} peaks are present at 475, 570, 600, 962 and 1000–1130 cm^{-1}. Peaks at 630 and 3580 cm^{-1} correspond respectively to the librational and stretching frequencies of OH^- ions of HAP. The shoulder at 630 cm^{-1} coupled with a band at 730 cm^{-1} assignable to $P_2O_7^{4-}$ ion and another at 875 cm^{-1} assignable to HPO_4^{2-} ion [9, 13, 17] appear in the case of calcium-deficient hydroxyapatite. With the formation of stoichiometric HAP, the shoulder at 630 cm^{-1} changes into a well-defined peak coupled with the disappearance of the 730 cm^{-1} [9, 17] peak. With increasing additions of $Ca(OH)_2$ to TCP beyond 3 : 2 molar ratio (e.g. in T_3 and T_4), the intensities of i.r. bands corresponding to $Ca(OH)_2$ at 3660 cm^{-1} (OH stretch of $Ca(OH)_2$) and 875 cm^{-1} in the product increase in intensity indicating the presence of free unreacted $Ca(OH)_2$ and CaO in the product.

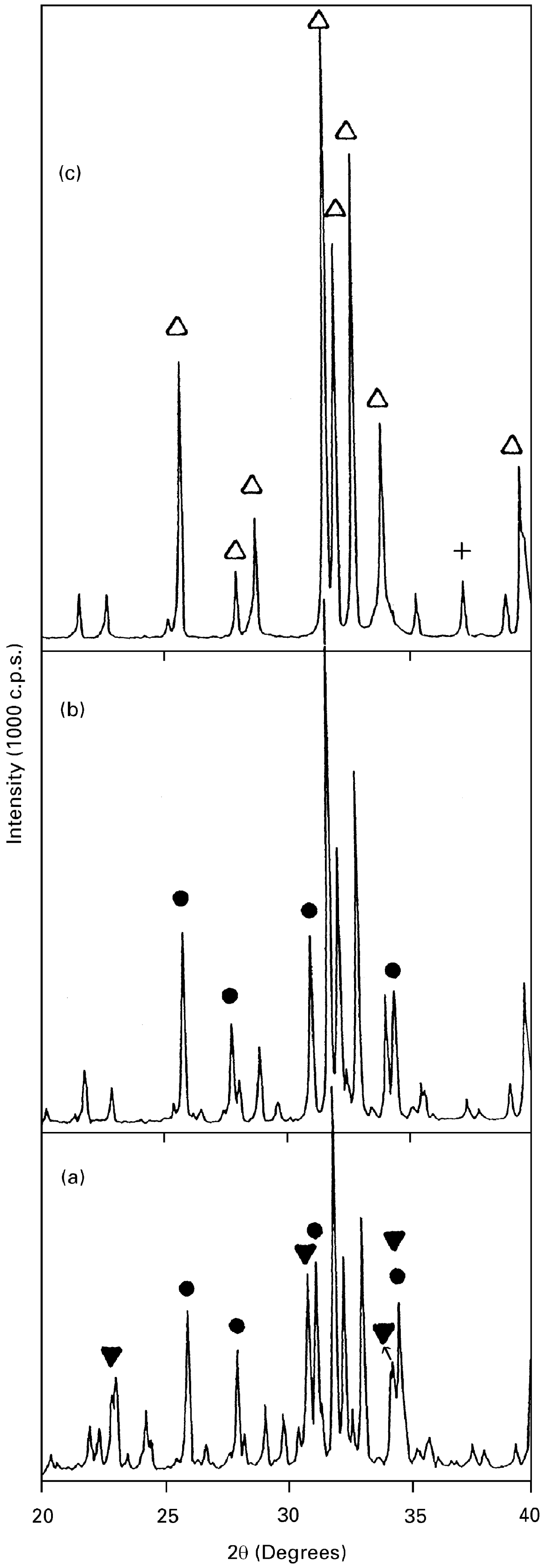


Figure 4 XRD spectra of TCP + $Ca(OH)_2$ mixture in the molar ratio of (a) 3 : 1; (b) 3 : 1.5; (c) 3 : 3, heat treated to 1250 °C for 2 h; (●) β-TCP, (▼) α-TCP, (△) HAP, (+) CaO.

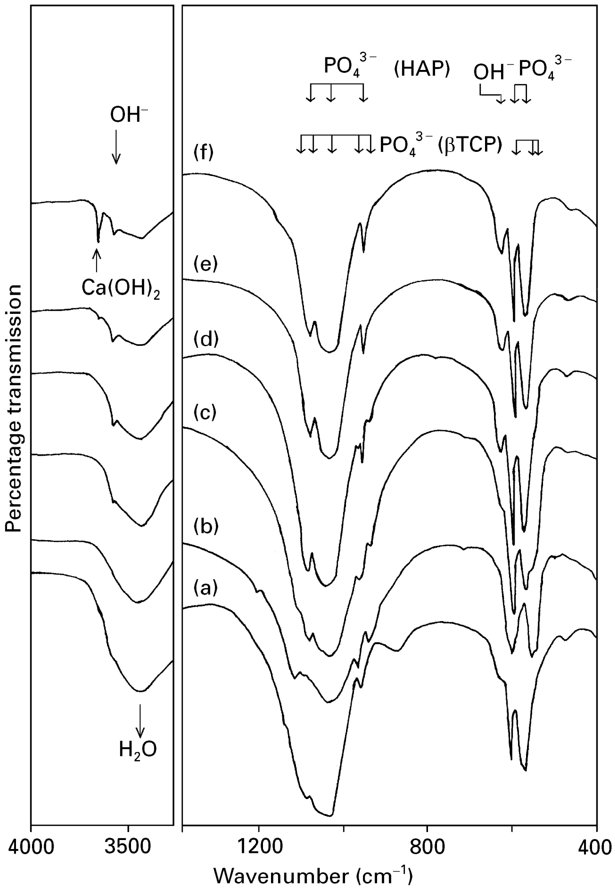


Figure 5 Infrared spectra of (a) as-received TCP powder and of products obtained from TCP + $Ca(OH)_2$ mixtures (in different molar ratios) on heat treatment at 1000 °C for 8 h; (b) 3 : 0; (c) 3 : 1; (d) 3 : 1.5; (e) 3 : 2; (f) 3 : 3 and 3 : 4.

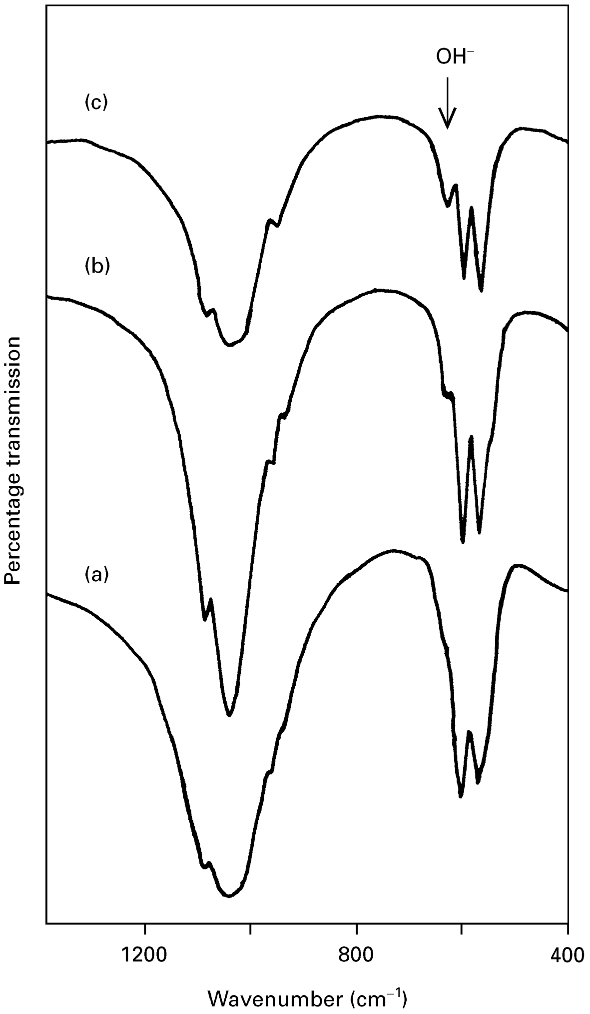


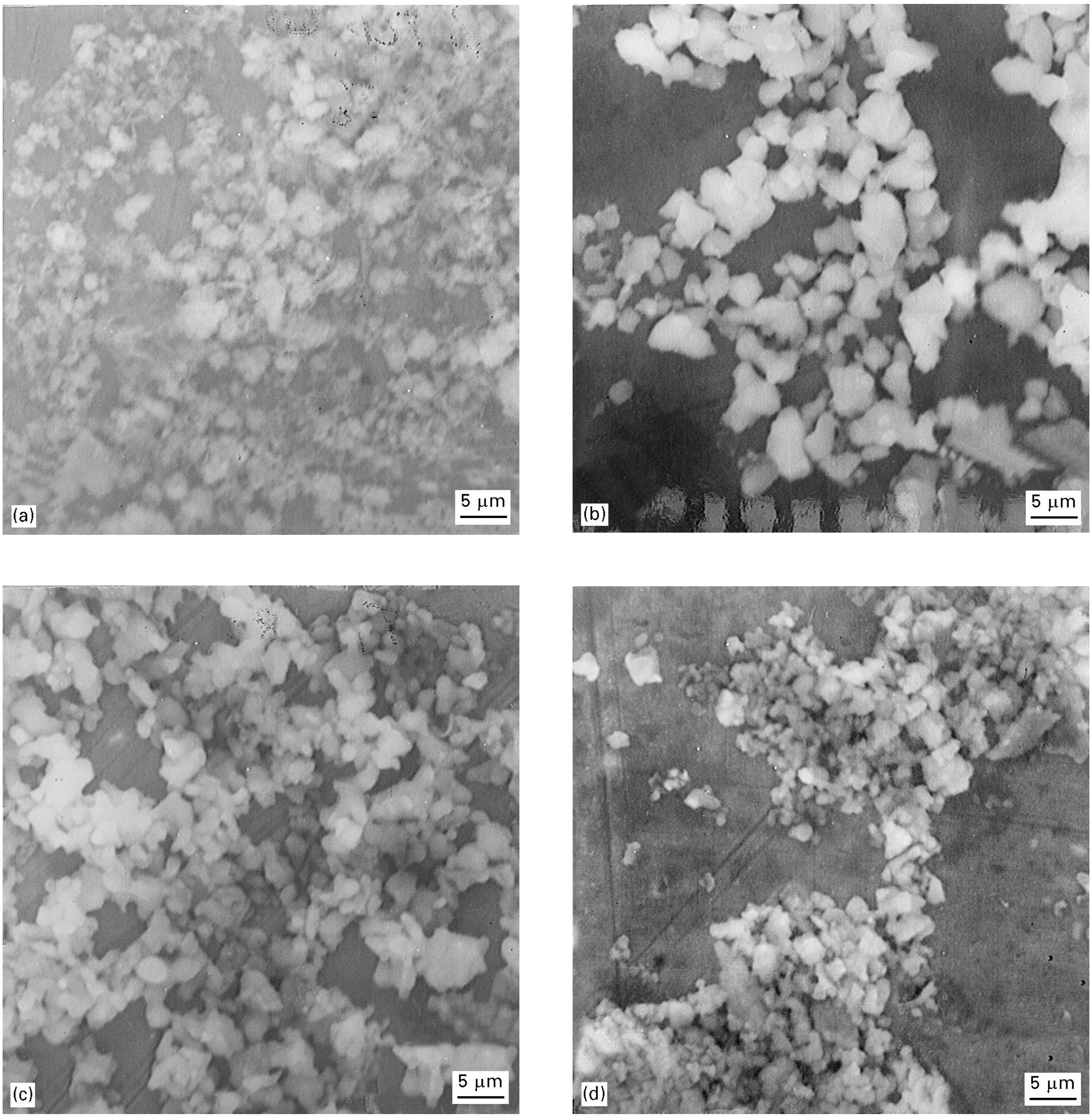
Figure 6 Infrared spectra of TCP + $Ca(OH)_2$ mixtures in different molar ratios (a) 3 : 1; (b) 3 : 1.5; (c) 3 : 2 heat treated to 1250 °C for 2 h.

3.2. Scanning electron microscopy of the samples T_0 to T_3

Scanning electron micrographs of the samples T_0, T_0 heat treated at 800 °C for 8 h ($T_0$800/8) and T_1–T_3 heat treated at 1000 °C for 8 h ($T_1$1000/8, $T_2$1000/8, $T_3$1000/8) are presented in Fig. 7. It is seen that sample T_0 consists of very fine primary microcrystalline particles (Fig. 7a) with certain areas of high agglomeration. Heat treatment up to 800 °C for 8 h gives rise to a fair amount of crystallization and grain growth and interparticular neck formation (Fig. 7b). Sample T_1 heat treated to 1000 °C for 8 h ($T_1$1000/8) gives a crystallized form of product (Fig. 7c) consisting of two types of particles, one as distinct crystallites and the other in the form of highly agglomerated product. These are probably a mixture of β-TCP and hydroxyapatite, as revealed by XRD and i.r. analysis. Sample T_2 heat treated at 1000 °C for 8 h ($T_2$1000/8) also gives rise to crystallites in highly agglomerated form (Fig. 7d), typical of hydroxyapatite phase, also observed by other earlier workers [13]. Sample T_3 heat treated to 1000 °C for 8 h ($T_3$1000/8) also presents a morphology similar to that of sample T_2 heat treated to 1000 °C for 8 h but with even a much larger extent of agglomeration (Fig. 7e) than T_2 case.

3.3. Particle size distribution of the samples T_0 to T_3

The particle size and particle size distributions of product powders T_0, T_1, T_2 and T_3, obtained on a sedigraph 5100 are presented in Fig. 8a–b. It could be seen that the original agglomerated powder T_0 has a median diameter (d_{50}, average particle size) of 8.8 μm while T_0 heat treated at 800 °C for 8 h ($T_0$800/8) has a median diameter of 4.7 μm. Samples T_1, T_2 and T_3 heat treated to 1000 °C for 8 h ($T_1$1000/8, $T_2$1000/8, $T_3$1000/8) have median diameters of 4.2, 19.4 and 18.5 μm, respectively. From this it could be seen that samples T_2 and T_3 which could be considered to be 100% hydroxyapatite have median diameters of 18–20 μm as against T_0 and T_1 whose median diameters are around 4–8 μm. This implies that on total conversion to 100% hydroxyapatite the samples become crystalline as well as agglomerated, and this is directly supported by the SEM pictures of Fig. 7. On altering the pH of the sedimenting medium from its value of 10.3 to 8.8 and 5.6 the median diameters of T_2 1000/8 change from 19.4 μm to 6.3 μm and 7.6 μm, respectively (Fig. 8b). This indicates that the size of the agglomerates could be broken down by diminishing the surface charge effects due to OH^- groups of HAP which are responsible for



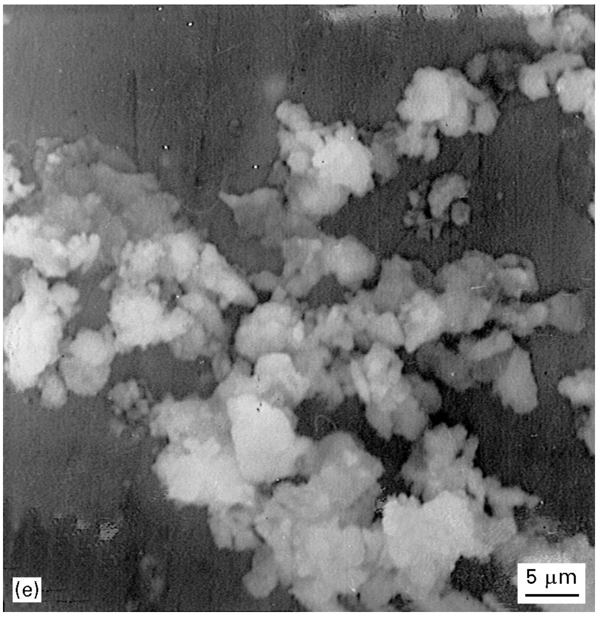


Figure 7 Scanning electron micrographs of (a) starting TCP (T_0) powder; (b) T_0 heat-treated at 800 °C for 8 h ($T_0$800/8); (c) heat-treated product of TCP + $Ca(OH)_2$ in the molar ratio 3:1 ($T_1$1000/8); (d) heat-treated product of TCP + $Ca(OH)_2$ in molar ratio 3:2 ($T_2$1000/8); and (e) heat-treated product of TCP + $Ca(OH)_2$ in molar ratio 3:3 ($T_3$1000/8).

agglomeration. From the SEM pictures it is anticipated that the primary particles of these agglomerates of HAP could be much finer. Presentation of these HAP powders in an appropriately buffered medium with suitable dispersing agents should help to preserve it in a finely dispersed state.

The sintering behaviour of these powders as well as the mechanical characterization of sintered products is presently under study and these will be reported elsewhere subsequently.

4. Conclusion

The results of the heat treatments given to the as-received, wet-milled, slip-cast discs of TCP (T_0) as well

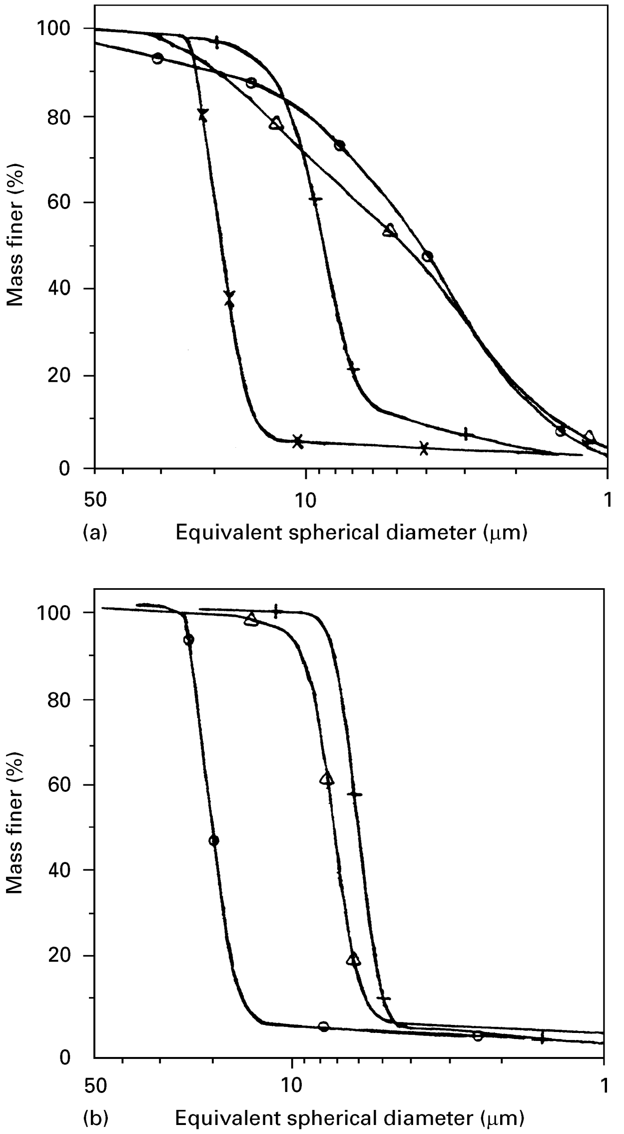


Figure 8 (a) Particle size distribution curves for: (+) starting TCP (T_0) powder; (△) T_0 heat-treated at 800 °C for 8 h ($T_0$800/8); (○) heat-treated product of TCP + $Ca(OH)_2$ in the molar ratio 3 : 1 ($T_1$1000/8); and (×) heat-treated product of TCP + $Ca(OH)_2$ in the molar ratio 3 : 2 ($T_2$1000/8). (b) Particle size distribution curves for heat-treated (1000 °C for 8 h) powder products of TCP + $Ca(OH)_2$ in the molar ratio 3 : 2 ($T_2$1000/8) at different pH values: (+) = pH 8.8, (△) = pH 5.6, (○) = pH 10.3.

as its mixtures with $Ca(OH)_2$ in various proportions (T_0, T_1, $T_{1.5}$, T_2, T_3 and T_4) at various temperatures in the range 600–1000 °C, are presented. Heat treatment at the temperature of 1000 °C/8 h transforms them into stable products consisting of either pure β-TCP, pure HAP or mixtures of HAP + β-TCP or HAP + CaO depending upon the extent (x) of $Ca(OH)_2$ ($0 < x < 4$) used for the reaction. Very high percentage of $Ca(OH)_2$ addition (e.g. in T_4) leads to the presence of excess $CaO/Ca(OH)_2$ in the HAP product phase which would be harmful for sintering and achieving good mechanical properties of the HAP formed. While pure HAP formed from T_2 is stable even at temperatures higher than 1000 °C (1250 °C/2 h heat treatment), the percentage of HAP formed from other compositions decreases with increase in the extent of formation of β-TCP (T_1 and $T_{1.5}$ cases) or CaO (T_3 and T_4 cases). The method is, therefore, suitable for the preparation of pure stoichiometric β-TCP, or HAP as well as their biphasic (HAP + β-TCP) composite powder mixtures.

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