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Synthesis and processing of hydroxyapatite ceramic tapes with controlled porosity

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) ceramic sheets with a wide range of porosities (up to 62%) have been prepared. The process is based on the reaction between dicalcium phosphate ($CaHPO_4$) and calcium carbonate ($CaCO_3$). When mixed with the appropriate Ca/P ratio, this proves to be a reliable new method for obtaining hydroxyapatite. Moreover, $CaCO_3$ serves as a gas-forming agent (due to the evolution of carbon dioxide and water during the reaction), which leads to the development of highly porous microstructures. Alternatively, $CaHPO_4$ and $CaCO_3$ can be reacted by calcining at 1000 °C to produce pure hydroxyapatite powders. When processed in a similar way, a dense ceramic results. By mixing 50 vol% of $CaCO_3$ and $CaHPO_4$ with precalcined powders, hydroxyapatite with an intermediate porosity was obtained. Moreover, it should be possible to achieve porosity control by mixing different amounts of uncalcined and precalcined powders. All of these powders are colloidally processed using tape casting to produce thin sheets 150–200 μm thick. This technique can be used to make laminates, with or without porosity gradients, up to several millimetres thick.

1. Introduction

Hydroxyapatite (HAp) ceramics are of considerable interest for clinical applications due to their high biocompatibility with bone and tooth tissue [1]. Among the many properties of these materials which contributes to their performance, porosity control plays an important role, both to promote osteoconduction [2] and to allow the design of ceramics with optimized structures, such as dense–porous layered structures [3]. Thus, there is an incentive to develop processing techniques for the production of HAp films and laminates with controlled porosity in each layer.

One established method for producing ceramic sheets and laminates involves tape casting. This technique has been used for many years in the electronic ceramics industry for the manufacture of capacitors and substrates [4, 5], and has been more recently developed for use in the production of structural ceramics [6, 7]. In principle, it should be possible to prepare HAp directly by type casting HAp powders. However, the commercial powders currently available are not well suited to colloidal processing methods such as tape casting. Moreover, HAp powders are chemically unstable at certain pH levels and tend to decompose over time, leading to variability in results depending upon the initial state of the powders. More reproducible results can be obtained, and at lower powder costs, by using other calcium phosphate compounds as starting materials which, through appropriate chemical additions and heat treatment, can be converted into HAp during processing. In this study, we have used dicalcium phosphate as a starting powder. This material is chemically stable and commercial powders exhibit a particle size distribution well suited to the application of colloidal processing technology.

The development of highly porous ceramic bodies requires the use of special techniques, since traditional ceramic processing methods usually result in porosities less than about 20%. Highly porous ceramic foams can be produced by the deposition of powders or precursors onto polymeric foams [8–10]. Alternatively, high levels of porosity can be obtained by foaming *in situ*, for example through the production of gas bubbles in a slurry or a glass [11]. We have adopted a variation of the latter approach in which a gas producing fugitive agent is used. In the current study, calcium carbonate has been used for this purpose since it can also be used to promote the formation of HAp during processing. As the $CaCO_3$ reacts with $CaHPO_4$ to produce HAp, both CO_2 and water vapour are produced. However, this gas is generated only within the green ceramic body (i.e. not in the presence of a liquid phase). It can only be expected to enhance porosity development therefore, by promo-

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ting a de-sintering reaction under the internal pressures generated inside the pore network. Moreover, considerable void space is left behind by the $CaCO_3$ particles. Some water vapour is also expected to be released as the dicalcium phosphate decomposes at around 430 °C. However, this is still above the temperature at which all of the liquid is removed from the system. In this paper, we describe a method for producing pure HAp sheets of controlled density, starting from a mixture of dicalcium phosphate and calcium carbonate.

The Ca/P ratio for pure HAp is 1.67, while that for dicalcium phosphate is 1. Therefore, the Ca/P ratio must be increased, and this can be achieved through the addition of calcium carbonate, with the following reaction expected upon heat treatment:

$$6CaHPO_4 + 4CaCO_3 \xrightarrow{1000\,^{\circ}C} Ca_{10}(PO_4)_6(OH)_2 + 2H_2O + 4CO_2$$

A $CaHPO_4/CaCO_3$ molar ratio of about 1.5 is required to produce pure stoichiometric HAp. Moreover, as the reaction shows, $CaCO_3$ generates substantial quantities of carbon dioxide during the reaction. Accordingly, porous structures should result from this reaction.

2. Processing of hydroxyapatite sheets

Tape casting is used to produce thin films (~ 200 μm) of hydroxyapatite. Essentially, this method entails the dispersion of a ceramic powder in (typically) a non-aqueous solvent, followed by the addition of plasticizers and binders which control the viscosity of the slip and provide strength and flexibility to the tape following drying. This slurry is then spread or "cast", by means of a doctor blade, onto a glass plate (Fig. 1). The "tape" thus produced, once the solvents have evaporated, contains 50–60% ceramic powders by volume, the remainder being made up of polymers and a small amount of porosity. The tape at this stage is flexible and can usually be removed without difficulty from the glass plate. Green tapes, so produced can either be fired singly, to produce thin dense ceramic films (~ 200 μm thickness), or laminated with other tapes and fired, in order to produce bulk ceramic sheets (up to several millimetres thick). The process is illustrated by means of a flowchart in Fig. 2. A more detailed description of the development of tape casting technology in this laboratory can be found elsewhere [7, 12].

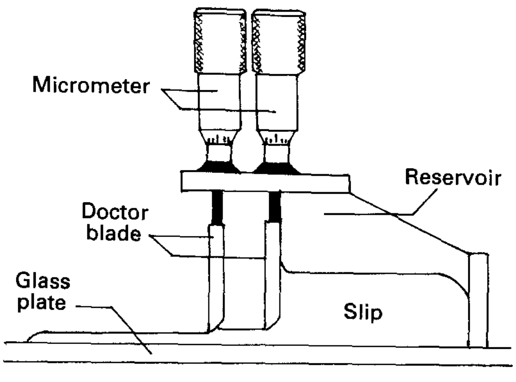

Figure 1 Schematic representation of a doctor blade and the tape casting technique [7].

In order to obtain stoichiometric hydroxyapatite, a 3:2 molar mixture of dicalcium phosphate and calcium carbonate were mixed by ball milling for 24 h, using alumina media. In the production of porous materials this was the starting configuration. However, for the development of ceramics with intermediate or low porosities, a further set of processing steps was required. For low porosity samples, this involved milling the powders with distilled water, and calcining the mixed powder for 2 h at 1000 °C. This temperature is sufficient to complete the conversion of the powder to pure hydroxyapatite, as shown below. This powder was then further ball milled for 6 h. For intermediate porosities, a portion of precalcined powder was added to the uncalcined powder mixture, and ball milled for 24 h, as above.

Particle size analysis (Horiba Capa-700 Particle Analyzer) on the as-received powder mixture showed a bimodal distribution with peaks at 0.5 and 2 μm, with a specific surface area of $3.6\ m^2\,g^{-1}$. The precalcined powders showed a more uniform distribution around 2 μm, with a specific surface area of $5.7\ m^2\,g^{-1}$. The $CaCO_3$ powders are considerably coarser, with an average particle size close to 10 μm.

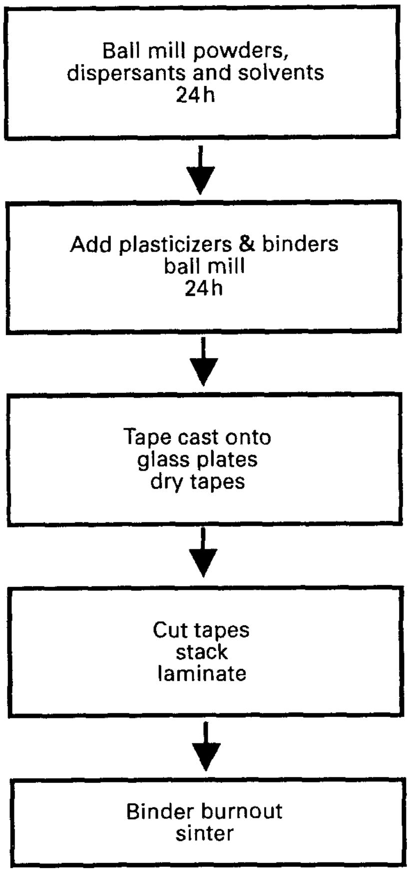

Figure 2 Flowchart of the tape casting processing method.

TABLE I Slurry formulations

Constituent	Amount		Function
	cm^3	g	
$6CaHPO_4 + 4CaCO_3$ as received or	100	241.8	Ceramic powder
precalcined powders	100	316	
Phosphate ester uncalcined powders with	2.5	2.63	Dispersant
precalcined powders	4.0	4.20	
Trichloroethylene (72 wt %) + ethanol (28 wt %)	213.3	251.7	Solvents
Polyvinyl butyral (PVB)	19.6	21.2	Binder
Dioctyl phthalate (DOP)	19.6	19.2	Plasticizer
Polyethylene glycol (PEG)	16.2	18.3	Plasticizer

However, these powders are refined considerably during mixing with dicalcium phosphate. It is therefore not possible to determine an accurate size for this power during firing.

The slurry formulation used in this work was based on that developed for tape casting of Al_2O_3 and Al_2O_3/ZrO_2 powders [7], and adapted to the current case. Dynamic viscosity measurements (Bohlin Visco 88BY viscometer) were used to determine the optimum dispersant concentration, defined as the concentration yielding the lowest viscosity for a given solids loading. The formulation used is given in Table I.

The tape casting slurry was made by first ball milling the powders, solvents and dispersant for at least 24 h. The polymers (i.e. binder and plasticizers) were then added, and the slurry was milled for another 24 h. Tape casting was accomplished using a moving doctor blade system consisting of two blades, with the blade speed set at 43 mm s^{-1}. The separations from the glass surface were 450 and 400 μm for the first and second blades, respectively. Once prepared, the tapes were allowed to dry for 24 h and then stripped from the glass surface.

Good quality tapes were obtained for both the uncalcined and precalcined powders, with tape thicknesses ranging between 150 and 200 μm. In the case of the uncalcined powders, segregation of particles to the surface of the tapes was observed during drying on the glass plate. This can be expected due to the differences in particle size between the starting powders used in the stoichiometric mixture.

3. Sintering and characterization

Two-stage firing cycles (in air) were used throughout this study. In the first stage, samples were heated slowly, at 30 °C h^{-1} to 400 °C, and held for 2 h. Previous work [7] has shown that the polymers used in this system burn in air at temperatures below 400 °C. Slow heating is required to minimize the potential for cracking due to gas pressure build up, while a 2 h hold is used to ensure complete combustion of all polymers. This was followed by a more rapid temperature rise, 300 °C h^{-1} up to the sintering temperature of between 850 and 1200 °C, followed again by a hold for 2 h. Despite the differences in starting powders and sintering conditions, X-ray diffraction analysis showed the presence of only one phase (pure hydroxyapatite) for all the samples. This is shown in Fig. 3 for the case of the porous tapes. The higher background level observed following sintering at 850 °C suggests that the reaction may not be complete after 2 h, although the only crystalline phase detected is HAp.

The density following firing is listed in Table II. For all the samples, density was calculated from the measured weight and dimensions of the sintered pieces. The measured sample densities are normalized by the density of stoichiometric hydroxyapatite, 3.16 g cm^{-3} [14]. The uncalcined powders produce very low sintered densities, ranging from 38–46% as the temperature rises. In contrast, samples made using precalcined powders are of high density, 92.8%. Samples made with 50 vol % precalcined powders resulted in an intermediate density of 70.5%.

The microstructures of the sintered bodies are shown in Figs 4 and 5. For materials made using uncalcined powders, a highly porous microstructure is achieved (Fig. 4). At the lowest sintering temperatures the scale of porosity is found to be several times that of the particles, around 2–3 μm (Fig. 4a). As the sintering

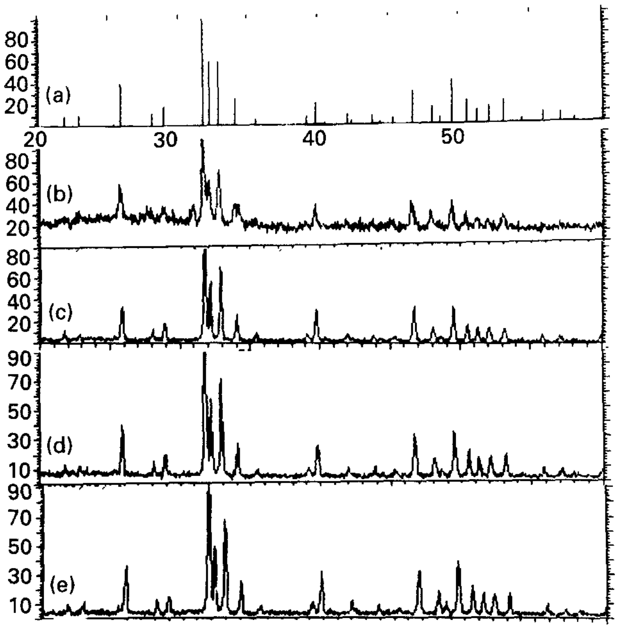

Figure 3 Power X-ray diffraction analysis of a porous tape, after heat treatment for 2 h at (b) 850 °C, (c) 1000 °C, (d) 1100 °C and (e) 1200 °C, as an example of phase characterization, compared to the JCPDS [13] standard of hydroxyapatite.

TABLE II Relative densities of the tapes

Starting powders	Sintering temperature (°C)	Relative density
Uncalcined	850	0.38 ± 0.03
	1000	0.408 ± 0.006
	1100	0.424 ± 0.001
	1200	0.464 ± 0.001
Precalcined	1200	0.928 ± 0.004
50 vol % mixture	1200	0.705 ± 0.002

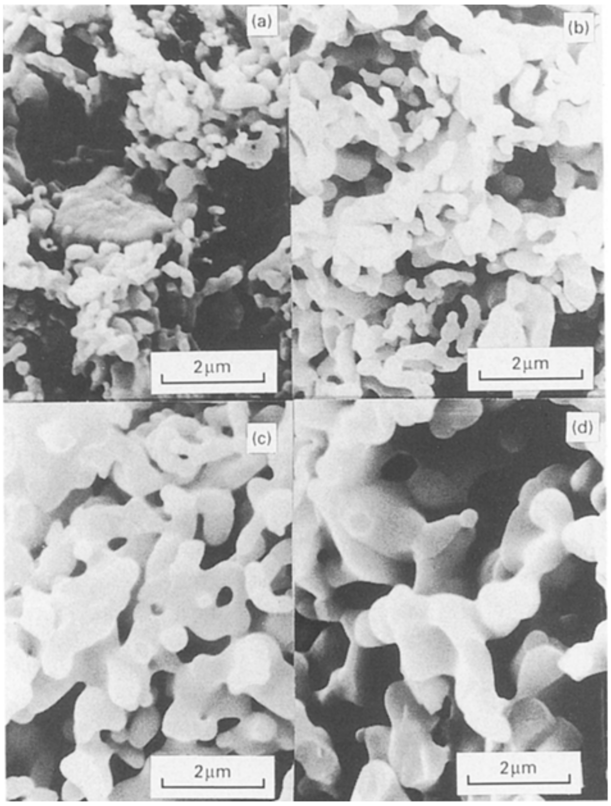

Figure 4 SEM images of fracture surfaces of porous tapes after sintering at: (a) 850 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C.

temperature is increased, particle coalescence and grain growth are observed, along with extensive interparticle neck formation. One might therefore expect the strength of this material to increase with sintering temperature. This is currently under study and will be reported elsewhere. The scale of the porosity does not change significantly with sintering temperature. In Fig. 5, the microstructure of tapes produced using different starting powders are compared. Sintering of precalcined-powder tapes at 1200 °C results in a high density hydroxyapatite ceramic, with some porosity evident in both the fracture surface (Fig. 5c) and the as-sintered surface (Fig. 5f). A fine-grained material was achieved, and the grain size of about 1 µm is similar to that found using the uncalcined-powder tapes (Fig. 5a and 5d) when both are sintered at 1200 °C. An intermediate density is observed for the tape made from the mixture of uncalcined and precalcined powders (Fig. 5b and 5e), when compared with the other two.

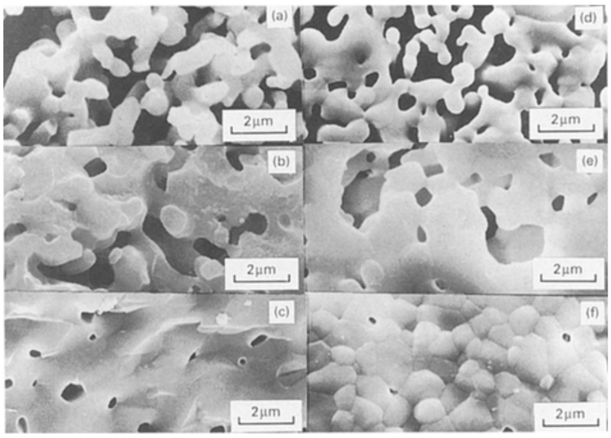

Figure 5 SEM micrographs of fracture surfaces of samples sintered at 1200 °C for 2 h from (a) uncalcined powders; (c) precalcined powders and (b) 50 vol % mixture; (d), (f) and (e) surfaces of the same sample as (a), (c) and (b), respectively.

3. Discussion

In this preliminary study, we have clearly demonstrated that pure hydroxyapatite with a wide range of porosity can be produced from a mixture of dicalcium phosphate and calcium carbonate powders. This material has so far been produced only as thin sheets (150–200 µm thick) from single tapes. However, the technology for producing much thicker pieces by lamination is well established [7, 12]. Moreover, complex shapes can be produced by green forming of laminates prior to firing [12].

The composition of the final tapes was consistent and reproducible, indicating complete reaction of $CaCO_3$ and $CaHPO_4$ to form hydroxyapatite. Moreover, the composition is identical for the porous tapes (in which case conversion is achieved during the firing cycle), and for the dense tapes (in which case conversion is achieved by precalcining), as well as for the tape with an intermediate density (which is a combination of the two former processes).

Similar slurry formulations were used for both processing methods, which produced tapes of high quality in all cases. However, some segregation of particles was observed for the uncalcined powders. As mentioned before, this might be due to differences in the powder size and morphology of dicalcium phosphate and calcium carbonate. Viscosity measurements were performed for both uncalcined and precalcined powders, in order to optimize the tape casting conditions. It was found that more dispersant was needed in the latter, which is consistent with the fact that these powders have a larger specific surface area. Previous work [7] has shown that there is a minimum amount of organic phase needed in order to remove tapes from the glass plate and that this amount depends on particle size (and perhaps morphology). Tape flexibility, on the other hand is primarily a function of the ratio of plasticizer to binder. Work aimed at developing a modified slurry formulation to prevent segregation of particles and to promote higher sintered density, for the uncalcined and precalcined powders, respectively, is now underway.

The density of the tapes made from uncalcined powders in very low, about 35%. Indeed, this is less than the powder density in the green tapes which is around 50%. Thus an increase in porosity must result during the reaction of the two powders to produce hydroxyapatite. Two complementary mechanisms are possible. Since the reaction takes place at low temperatures (below 850 °C) when the body has very little strength, the pressure created by the gases formed during the reaction could result in some de-sintering. In addition, there is weight loss of around 18 wt% during the reaction, which was detected using thermogravimetric analysis (TGA). Most of the space occupied by the $CaCO_3$ particles is turned into porosity. The amount of $CaCO_3$ is fixed with respect to dicalcium phosphate by the Ca/P ratio required. However, both the uncalcined $6CaHPO_4$–$4CaCO_3$ mixture and the corresponding precalcined powder give pure hydroxyapatite as final product. This allowed the production of the tape with an intermediate density, and it should be also possible to mix $CaHPO_4$, $CaCO_3$ and precalcined powders in various proportions in order to produce materials with controlled densities ranging from 35 to about 100% of theoretical.

The scale of the porosity is relatively insensitive to the sintering temperature (Fig. 4), but is likely to depend on the powder size. In particular, finer $CaCO_3$ particles would produce smaller pores [11]. Thus it should be possible to tailor the scale of the porosity by adjusting the $CaCO_3$ powder size so long as good power mixing can be achieved.

We conclude by offering some speculative remarks on the potential of this technology for producing a range of hydroxyapatite components. In addition to the ability to tailor the density as just described, it is also possible to develop functionally gradient materials in which the porosity is varied as a function of depth through a component. The tape casting and lamination process is ideally suited to this since green tapes with different ratios of calcined to uncalcined powders can be made. These can then be laminated together in any desirable arrangement. In particular, one could make pieces with porous interiors and a dense surface layer, or vice versa. An alternative approach to the development of a porous coating might involve dipping a component into a slurry with a formulation similar to that used for tape casting. Finally, we note that laminates can be formed into complex shapes prior to forming [12]. This is done at modest temperatures (~ 100 °C) by pushing a laminated sheet into a die cavity.

5. Conclusions

In this preliminary study of the production of hydroxyapatite with controlled porosity we have shown that:

(i) Tape casting is a promising technique for the preparation of bioceramic tapes.

(ii) Pure, stoichiometric HAp tapes can be produced through the reaction of $CaHPO_4$ and $CaCO_3$.

(iii) High porosity HAp results when tapes made from $CaHPO_4$ and $CaCO_3$ are fired at temperatures above 850 °C. $CaCO_3$ provides a fugitive gas generating species which not only enables the development of hydroxyapatite but also promotes porosity development.

(iv) High density HAp results when tapes made from precalcined powders are fired at 1200 °C.

(v) Intermediate porosities can be achieved by mixing uncalcined and precalcined powders.

(vi) Optimization of the slurry formulation and better particle size control of the precalcined powders are necessary to improve the quality of the final products.

Many potential biomedical applications can be developed due to the possibility of producing graded microstructures through lamination of multiple tapes, and through the fabrication of complicated shapes by green forming of such ceramic laminates.

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