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Morphology and structural characteristics of hydroxyapatite whiskers: Effect of the initial Ca concentration, Ca/P ratio and pH

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ABSTRACT

Hydrothermal homogeneous precipitation combines the best characteristics of the hydrothermal and homogeneous precipitation methods, and allows long and uniform hydroxyapatite (HA) whiskers, with a high aspect ratio and high crystallinity, to be obtained. Their morphology and structural characteristics depend on the initial Ca/P ratio (iCa/P) and pH (ipH), as well as the initial calcium concentration (i[Ca]). Variation in these values had no effect on constitution, which was crystallographically indistinguishable from HA. Ca/P ratio steadily improved with increases in both ipH and iCa/P, but was independent of i[Ca]. Uniform whiskers were obtained at high iCa/P and low ipH, or at high ipH and low iCa/P. Whiskers with a mean length of 96–140 μm and an aspect ratio of 96–136 were obtained at ipH = 2–3 and iCa/P = 1.67–2. At a low ipH and low iCa/P, irregular plate-like particles and branch-like whiskers were formed, while a high ipH favoured the formation of lath-like HA at high iCa/P. Preferred growth along the *c*-axis was more intense at higher iCa/P and ipH as well as at low i[Ca]. However, under these conditions, the crystal growth habit was also changed, showing preferred growth along both the *c*- and *a*-axes. The increase in whisker width over the general value obtained was abrupt at low i[Ca] and high iCa/P.

1. Introduction

Reinforcement by whiskers has been considered an effective way to improve the mechanical properties and reliability of biomedical ceramics and composites due to their unusually high tensile strength and remarkable characteristics [1,2]. To attain the strength and bioactivity required for clinical use, calcium phosphate-based whiskers or fibres show promise, while the occupational health issues associated with airborne, supposedly bioinert, ceramic whiskers and fibres are obviated during manufacture and handling [3–5]. The use of hydroxyapatite (HA) whiskers has attracted much attention in recent decades in a wide range of formulations and experimental conditions.

HA whiskers have been prepared by a variety of methods [6–13], amongst which the wet chemical routes, including homogeneous precipitation [9,10], dissolution and recrystallization [14], decomposition of Ca-chelate [15,16] and the hydrothermal method [13,17], offer relatively easy procedures for mass production. However, crystal growth depends greatly on the properties of the starting solution, and both the constitution and morphology of whiskers have been found to be greatly affected by the initial concentrations of calcium (i[Ca]) and phosphate (i[P]), the initial Ca/P ratio (iCa/P) and pH (ipH), and the reaction temperature. Fibrous HA grown in agar gel gave a zigzag-, straight- or needle-like morphology, depending on the ipH [6]. The Ca/P ratio and fibre length from homogeneous precipitation using urea were found to increase with the iCa/P ratio at fixed i[P] [10], but their width decreased; the crystals were highly strained, and the carbonate content of the products (from the urea hydrolysis) increased with the Ca/P ratio of the product. For preparation from buffer solutions of calcium acetate in the presence of phosphate [18], the phase composition and morphology of the products also varied with ipH and iCa/P. HA whiskers were only obtained from solutions with iCa/P = 1.56–3.7 and ipH = 4.8–5.0. At ipH < 4.8 and iCa/P < 1.56, monetite, formed due to low pH and release of H^+ ions during the reaction, would accompany the whiskers.

Whiskers prepared by most of the above methods are generally deficient in Ca, with low aspect ratio and thermal stability. In the case of synthesis via the hydrothermal reaction of a calcium chelate with phosphate ions, although fibrous HA with a length of over 150 μm and an aspect ratio of 20–60 could be obtained by optimising the initial concentration and iCa/P, the aspect ratio decreased with increasing iCa/P [19]. Unfortunately, no systematic study of these factors has been reported. Thus, despite much effort to improve the quality of HA whiskers, well-crystallized whiskers

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with a uniform morphology and a high aspect ratio are difficult to obtain using these techniques because of the sensitivity to the preparation conditions [20,21]. Furthermore, the poor dispersibility of such material due to entanglement or agglomeration becomes a problem when mixing with matrix materials, and the reinforcing efficacy is low due to the low aspect ratio and short length [22,23]. Such whiskers rarely satisfy the requirements for reinforced biocomposites.

Hydrothermal homogeneous precipitation combines the best characteristics of the hydrothermal and homogeneous precipitation methods, and in this way long HA whiskers with a high aspect ratio and uniform morphology have been successfully prepared in the presence of acetamide (AA), as we have previously reported [24,25]. AA hydrolyses slowly under hydrothermal conditions compared with the more commonly used urea, allowing better and easier control, with rapid nucleation and growth, at low supersaturation, of (most importantly) uncontaminated whiskers. Both length and width increased with decreasing i[Ca] and i[P]. Whilst long, uniform whiskers with a high aspect ratio were obtained for i[Ca] = 21–84 mmol L^{-1} at the chosen iCa/P of 1.67, it was apparent that the product description was strongly dependent on the starting concentrations. However, there are no prior reports on the effects of iCa/P and ipH under various i[Ca]s using AA as a precipitation agent under hydrothermal conditions to guide optimisation. Thus, the present aim was to elucidate their effects in more detail so as to identify, if possible, optimum conditions.

2. Experimental procedure

2.1. Preparation

Aqueous solutions containing Ca and PO_4 were prepared first by dissolving the analytical grade reagents $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ in 0.05 mol L^{-1} HNO_3 (all AnalaR, BDH, Poole, UK), to give 21, 33, 42, 52 and 63 mmol L^{-1} Ca. The initial PO_4 concentration, i[P], was varied to obtain iCa/P ratios of 1, 1.33, 1.5, 1.67 and 2 for each i[Ca]. The concentration of acetamide (99%, Alfa Aesar, Heysham, Lancashire, UK) was maintained at 1 mol L^{-1}. The solutions were adjusted to an initial pH of 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 with 0.1 mol L^{-1} HNO_3 or 1:1 ammonium hydroxide before processing.

The hydrothermal processing was in aliquots of 100 ml of a solution in an autoclave, as reported previously [24]. After processing at 180 °C for 10 h, the mixture was allowed to cool naturally to the ambient temperature over 12 h. The product was then filtered and washed quickly four times with deionized water, and dried in air at 80 °C.

2.2. Characterisation

The product was characterised using X-ray powder diffraction (XRD) (X'Pert Pro, PANalytical, Almelo, The Netherlands) with a

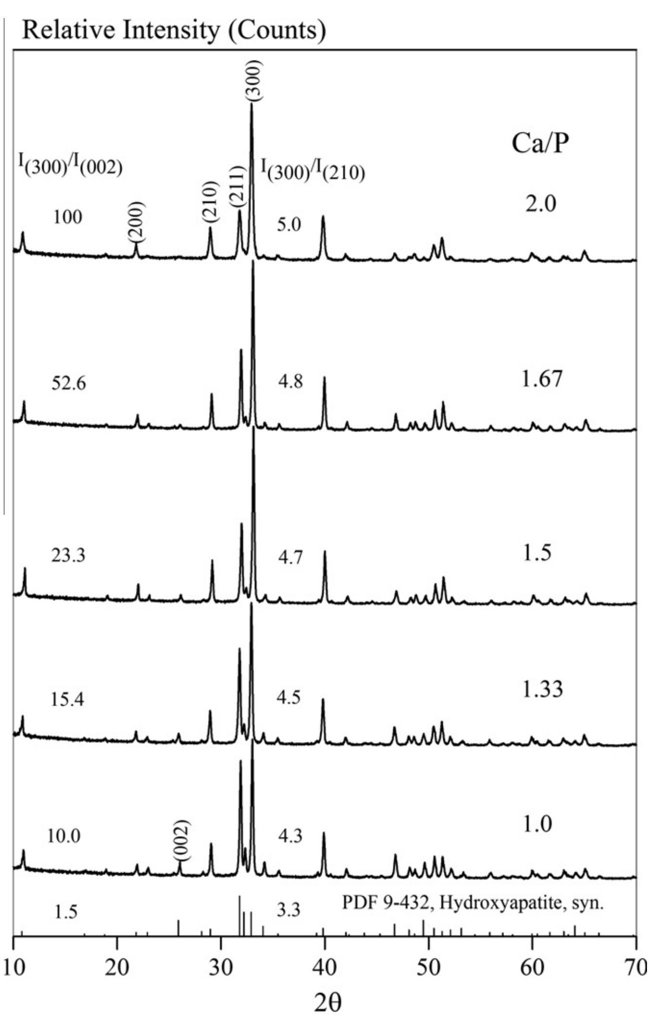

Fig. 1. XRD patterns of HA prepared at 180 °C for various iCa/Ps at ipH = 3.

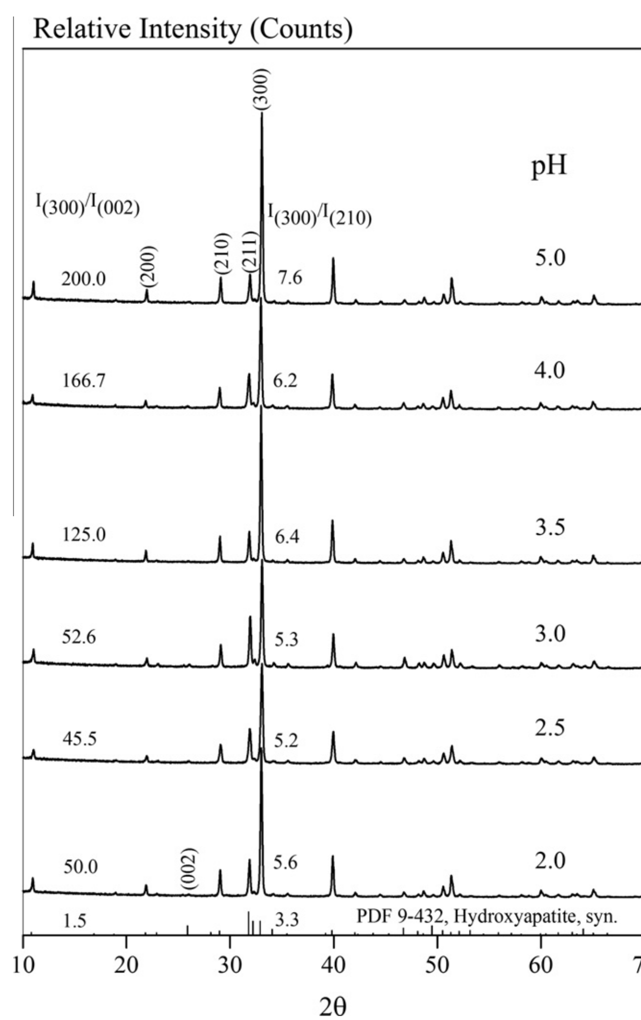

Fig. 2. XRD patterns of HA prepared at 180 °C for various ipHs at iCa/P = 1.67.