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Hydroxyapatite, fluor-hydroxyapatite and fluorapatite produced via the sol-gel method. Optimisation, characterisation and rheology

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ABSTRACT

Objectives. Currently, most titanium implant coatings are made using hydroxyapatite and a plasma spraying technique. There are however limitations associated with plasma spraying processes including poor adherence, high porosity and cost. An alternative method utilising the sol-gel technique offers many potential advantages but is currently lacking research data for this application. It was the objective of this study to characterise and optimise the production of Hydroxyapatite (HA), fluorhydroxyapatite (FHA) and fluorapatite (FA) using a sol-gel technique and assess the rheological properties of these materials.

Methods. HA, FHA and FA were synthesised by a sol-gel method. Calcium nitrate and tri-ethylphosphite were used as precursors under an ethanol-water based solution. Different amounts of ammonium fluoride (NH₄F) were incorporated for the preparation of the sol-gel derived FHA and FA. Optimisation of the chemistry and subsequent characterisation of the sol-gel derived materials was carried out using X-ray Diffraction (XRD) and Differential Thermal Analysis (DTA). Rheology of the sol-gels was investigated using a viscometer and contact angle measurement.

Results. A protocol was established that allowed synthesis of HA, FHA and FA that were at least 99% phase pure. The more fluoride incorporated into the apatite structure; the lower the crystallisation temperature, the smaller the unit cell size (changes in the a-axis), the higher the viscosity and contact angle of the sol-gel derived apatite.

Significance. A technique has been developed for the production of HA, FHA and FA by the sol-gel technique. Increasing fluoride substitution in the apatite structure alters the potential coating properties.

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1. Introduction

Titanium (Ti) and its alloys have long been recognized and used as dental and orthopedic implant materials. To improve the implant-tissue osseointegration, considerable effort has been exerted to modify the Ti surface structure both physically and chemically [1–3]. Hydroxyapatite [HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] coatings on Ti substrate have attracted significant attention for several years aimed at combining the excellent biocompatibility of HA and load-bearing ability of Ti [4,5]. Currently, most HA coatings are produced by a plasma-spraying technique [6,7]. In vivo reports on the system have shown good bone-bonding ability and fast osseointegration compared with pure Ti implants. This was mainly attributed to the osteoconductivity and chemical and biological similarities of HA with the human hard tissues [5,8,9]. There is some debate as to the actual requirements of a coating. There are two possibilities: (1) the coating has very low solubility and will remain in place for some considerable time (for the devices lifetime) and maintain a stable biological interface or (2) the coating is merely temporary and its role is to promote rapid growth of bone onto the surface of the coating but the coating will be replaced such that the bone will bond directly to the metal implant surface. This is of particular relevance to immediate loading implants. This is further complicated by the role of crystallinity. Lower crystallinity coatings showed faster resorption in a canine model and also higher levels of bone apposition onto the surface at 16 weeks, with mechanical fixation better in the lower crystallinity samples at 16 weeks but no difference at 32 weeks [10,11].

There are some parameters to be improved in the plasma spraying process, such as coating strength, chemical homogeneity, and residual porosity. These are related to the high fabrication temperature and coating thickness [7]. Recently, alternative methods have been developed to produce thin HA films. The sol-gel technique, being one of the thin film methods provides some benefits over the plasma spraying method, such as chemical homogeneity, fine grain structure, and low processing temperature [12]. Moreover, compared with other thin film methods, it is simple and cost efficient, as well as effective for the coating of complex-shaped implants. There are conflicting reports [13] which may be due to differing methodologies, but in general it is agreed that pure fluorapatite (FA, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) is known to have a much lower solubility than HA, because FA possesses a greater stability than HA, both chemically and structurally [13,14]. Moreover, the HA is able to form fluorhydroxyapatite (FHA, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_1\text{OH}_1$) with the crystallographic substitution of OH^- by F^- . Moreover this substitution has been shown to occur in aqueous solutions and is also irreversible [15]. Hence, modulation of the extent of fluoride substitution provides an effective way of controlling the solubility of the apatite which thus allows us to produce a wide range of coatings with differing biological properties. In practice, the fluoride ion itself has been studied widely in dental restorative areas, due to its advantages over other ions in that it can reduce the formation of caries in bacterially contaminated environments and promotes mineralisation and crystallisation of calcium phosphates in the formation of bone [14,16]. There is some conflict in the literature when com-

paring hydroxyapatite with fluorhydroxyapatite coatings. In unloaded models, a fluorine containing hydroxyapatite coating was shown to be more stable [7]. However, when loaded, no significant difference was seen [17,18], although both types of implants showed good stability. Interestingly in a human trial, the hydroxyapatite coating was considerably thinner than the equivalent fluorhydroxyapatite coating [19]. Nevertheless, there have been few reports concerning the fabrication or characterisation of the HA, FA or FHA materials produced via the sol-gel route and it was the purpose of this study to undertake this. Furthermore with reference to the literature, while use of triethylphosphite and calcium nitrate as precursors have been the most successful method for the production of HA via a sol gel [20–22], the majority of the materials produced via the sol-gel reactions are β -tricalcium phosphate (β -TCP) and not HA/FA/FHA and this study sought to optimise the production of phase pure apatites and investigate their thermal and rheological properties.

2. Materials and methods

2.1. Preparation of HA sols

16.16 g of triethylphosphite (TEP [$\text{P}(\text{C}_2\text{H}_5\text{O})_3$], Aldrich, USA) was hydrolysed for 72 h in a mixture of 33.12 g of ethanol and 5.04 g of distilled water (P containing solution, VWR, UK). This mixture was then added to a solution of 39.36 g calcium nitrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Aldrich USA] in 15.12 g of distilled water. A 5% (w/v) solution of ammonium hydroxide (NH_4OH , VWR, UK) was added to the solution in order to improve gelation and subsequent formation of an apatite structure. The solution was allowed to react for 24 h and then age for a further 24 h at room temperature.

2.2. Preparation of FHA and FA sols

The FHA sols were prepared using various amounts of ammonium fluoride (NH_4F , Aldrich, USA) in the P containing solution. The [P]/[F] molar ratios were 12, 6, 4 and 3 in order to have the corresponding compositions of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{0.5}\text{OH}_{1.5}$, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_1\text{OH}_1$, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{1.5}\text{OH}_{0.5}$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ by replacing the OH group with F ions in molar ratios of 0.25, 0.5, 0.75 and 1 respectively. After stirring for 72 h, the solutions were added slowly to a solution containing a stoichiometric amount (Ca/P ~ 1.67) of calcium nitrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Aldrich, USA] following the protocol developed for the HA sols.

2.3. Powder preparation

Following successful preparation of apatites via the sol-gel reaction, samples of the sol-gel derived materials were heated to 500, 600, 700, 800, 900 and 1000 °C for 2 h in air using a hot air oven (Lenton Furnace, Lenton Thermal Designs Limited, UK) with a ramp of 5 °C/min, dwell time of 60 min and cool down rate of 10 °C/min.

Following heating in the hot air oven the samples were ground to a powdery form for 20 min using a vibrating agate ball mill (Fritsch, Germany) and to ensure similar particle sizes $\sim 20 \mu\text{m}$ were passed through a sieve (Fritsch, Germany).

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