

Fabrication of Nano Crystalline Hydroxyapatite-Polymer Composite

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Statement of Purpose:

Hydroxyapatite chemical and structural similarity with the mineral phase of bone and teeth, synthetic hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAp), is widely used for hard tissues repair. The different clinical applications involve repair of bone defects, bone augmentation, as well as coatings for metallic implants. One of the most important requirements of a material designed for bone substitution and/or repair, is the ability to create a bond with the host living bone [1]. HAp has a high affinity for natural tissue *in situ* and can be molded to fill spaces created by physical damages of bones and/or teeth. It also has been an attractive material for chromatographic separation, catalysis and ion exchange apart from their use as bone and dental implants. The considerable development in the field of material science is inspired by the biological composite materials such as bones, teeth and shells because of their unusual structural, morphological, and mechanical properties. Such hybrid materials unlike synthetic composites are characterized by the high degree of organization of the inorganic phase. The HAp as well as other calcium phosphates shows poor mechanical properties (low elasticity and high brittleness). The combination of HAp with polymeric matrix leads to the hybrid materials exhibiting high flexibility, mechanical strength, biocompatibility, and good processing/sHAping [2]. The interaction of the HAp with polymeric matrix is realized by covalent bonds, hydrogen bonds, dipole-dipole interactions, or complexation of Ca^{2+} -ions by functional groups such as amine, acetylamine, or hydroxyl [3]. In this way, the polymeric matrix plays an important role in the nucleation and growth of HAp crystals and determines their size, morphology, and orientation in the composite material. The most important application fields for hybrid materials containing HAp are tissue engineering, implants, drug delivery systems, catalysis, adsorbents and protein chromatography. Among the alternative methods, sol-gel and synthesis of nano crystalline HAp has recently attracted much attention, due to its many advantages.

Methods:

Classical methods for HAp powder synthesis include direct precipitation, hydrothermal techniques, hydrolysis of other calcium phosphates, as well as solid-state reactions. Among the alternative methods, sol-gel and hydrothermal synthesis of HAp ceramics has recently attracted much attention, due to its many advantages, which include high product purity, homogeneous composition, and low synthesis temperature [4]. Moreover, the sol-gel process is easily applicable to surface coating, and it allows the preparation of high-quality HAp nanocomposite. Aging of the precursor

solutions was found to be critical in developing an apatite phase [5]. The speed of gelation, the chemistry of the precursors, and the nature of the solvent, are among the main factors affecting the process. The hydrothermal method has been found to be the suitable method to prepare well-crystallized and non-agglomerated crystals with homogeneous size, sHAp and composition that can be achieved even at low temperature [6]. HAp nanocomposite with different morphology were grown by hydrothermal method using different precursors like minerals, metals, polymer. The large variety of polymeric materials have been used as templates for the synthesis of HAp such as protein collagen[7], poly(L-lactic acid), poly(aspartic acid), alginates, gelatine, chitosan, chitin, dendrimers, hydrogels etc.,. The use of polymeric particles as templates for the growth of HAp nanocrystals has not been intensively studied. Polymeric particles as templates provide several advantages such as uniform size, extremely large surface area, and enormous possibilities for the surface functionalization. The starting materials used in the synthesis of hydroxyapatite were Calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Merck GR), Di-Potassium hydrogen phosphate anhydrous (K_2HPO_4 , Merck GR), Poly(ethylene glycol) (PEG) and Sodium meta silicate ($\text{Na}_2\text{O}_3\text{Si} \cdot 9\text{H}_2\text{O}$, Loba) was dissolved in 50ml of deionized water at 37°C under stirring. The concentrations of the reactants were varied in order to obtain a Ca/P molar ratio in solution of 1.00, 1.67, and 2.55. Before mixing, the pH value of the solutions adjusted above 9 with NH_4OH . The powder products were stirred for 3 min at 37°C . The filtered products were repeatedly washed, and dried at 37°C overnight. Gels were obtained by drying the sols after 3 min of stirring at 37°C . A part of the sol was dried at 37°C , whereas a second part was oven-dried at 80°C overnight.

Results:

The combination of (HAp) bioactivity and (polymer) toughness may result in a new load bearing bioactive material with good mechanical properties [8]. However, the increase of HAp content in the polymer is affected by the particle size and the interface between HAp and polymer which may also cause the change of mechanical strength of composite [9]. It has been also speculated that the smaller of the HAp particles, the higher of the HAp content in the composite, and the better the homogeneity of the composite. In an effort to introduce strong interfacial bonding between the two phases, nano-grade hydroxyapatite (n-HAp) crystals and polar polymer that may form chemical bonding with n-HAp should be selected to make nano-composite.

Conclusions:

Nanopolymer composite with high HAp content have good homogeneity and chemical interface bonding. When compared to natural bone, the synthetic nano-composite can be said to be a bone-like biomaterial, the n-HAp provides the bioactivity for the composite, forming bone-bonding with natural bone and the polymer is responsible for mechanical strength and toughness. Therefore the synthetic nano-composite may be one of the best bioactive materials for load-bearing bone repair or substitute and drug delivery applications. Interface binding and uniformly dispersion are important for enhancement of bioactivity and the mechanical property of the composite. The some invaluable polymers provide and opportunity to produce biomimetic materials for clinical applications.

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