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Convenient approach of nanohydroxyapatite polymeric matrix composites

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ABSTRACT

Polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) were used to prepare polymeric matrix composites of nanohydroxyapatite (HAV and HAP), respectively, by using a biomimetic approach under 100 °C. A comparison with synthetic nanohydroxyapatite prepared by precipitation (SHA) was evaluated. Characterization of the prepared powders by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was achieved, X-ray diffraction (XRD), scanning electron microscope (SEM) with elemental analysis by (EDS) and inductively coupled plasma-optical emission spectrometer were used. DTA and TG showed the weight loss in the 400–1200 °C was almost attributed to carbonate decomposition which appeared apparently in the polymer associated samples due to the decomposition of polymer matrix. X-ray diffraction confirmed mainly the formation of hydroxyapatite. Specific surface area (BET) and scanning electron microscope and scanning electron microscopy (SEM) confirmed the range of nanosized of the prepared HA samples. The polymer matrix prefers orientation of the particles to rod-like shape. Elemental analysis showed mainly, Ca, P, C and O ions besides Na and Cl. Inductively coupled plasma showed the composition and the Ca/P atomic ratio of all samples ranging between 1.72 and 1.85.

1. Introduction

Bioceramic is a branch of ceramic that supplies various kinds of biomaterials to fit in the field of dental and orthopaedic biomedical applications. The use of bone-substituted materials is imperative to repair and reconstruct diseased or damaged parts in hard tissue such as bone, hips, knees and teeth. The most common materials used in this field are hydroxyapatite. It is considered as ideal biomaterials due to its biocompatibility, bioactivity and chemical reactivity particularly for applications in the bony sites without high mechanical solicitations [1].

Hydroxyapatite (HA) has similar composition and crystalline structure to apatite in human skeletal system, and therefore, it is suitable for bone substitution and reconstruction [1]. Literature survey discusses the use of conventional HA in the form of powder, dense or porous blocks at the macroscale level [2,3]. Recently, nanohydroxyapatite attracts researchers as it plays a significant role in various biomedical applications due to its unique functional properties of high surface area to volume ratio and its ultra fine structure similar to that of the biological bone [4,5]. Extensive efforts have been made to produce synthetic nano-HA materials. Methods that have been used for preparing nano-HA materials included chemical precipitation [6], in some cases followed by spray drying [7], sol–gel approach [8], microemulsion techniques [9], precipitation from complex solutions followed by microwave heating [10], wet chemical methods incorporating a freeze-drying step [11] and mechanochemical synthesis [12]. In our previous work, nano-oxides and hydroxyapatite prepared through the urea-formaldehyde polymeric route [13–15]. This method revealed the possible substitution of the cations from aqueous solution in the structure of the resin formed to produce nanosized and homogenized product after heat treatment.

In the natural bone and teeth, the nanometer-sized HA crystal is embedded in the collagen matrix with an average length of 50 nm, width of 25 nm, and a thickness of only 2–5 nm [16]. In fact, collagen acts as a template in the controlled biomineralization process [17]. However, the poor mechanical properties of the synthesized HA, such as high elastic modulus and low fracture toughness restrict its applications. Thus, HA is used in composite form (HA–polymer). It has found application as sorbent for numerous heavy metals and radionuclides [18–20]. In addition, it can be used to retain useful bioactive properties as well as enhancement in mechanical properties. Meanwhile, the polymer matrix acts as a template that directs crystallization of calcium phosphates. This effect has a great relevance to the understanding of the biomineralization process [21,22]. Where, in the biomineralization process of bone and teeth, the nucleation and growth of inorganic crystals occur in the presence of biological macromolecules. It can interact

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with inorganic crystals by electrostatic and hydrogen bond effects. These effects play an important role in the morphology and grain size of the inorganic crystal. Besides, HA is a more stable phase, i.e. incredibly less resorbable as compared to other bioceramics such as tri-calcium phosphate [23]. The resorbability of HA can slightly be improved with some ceramic oxides and ionic doping agents or by adding polymer to form composite [24,25]. Therefore, synthetic composites have been used in the replacement of the natural bone through the essence of biomimicking approach. Thus, the molecular control over the morphology, size, and anisotropy of the inorganic crystals and their uniform distribution over the organic phase are some of the main goals aimed at in the biomimicking process. Polymers containing polar functional groups such as COOH, CH, CH_2, PO_4H_2, and OH have been found to be useful in this regard. These ionizable side groups provide a greater affinity to positive calcium ions and the nucleation of hydroxyapatite crystals in the solution [2,5].

Keeping the above points in view, we have chosen two types of polymer viz., polyvinyl alcohols (PVA) and polyvinylpyrrolidone (PVP) in this study. Polyvinyl alcohol is a low cost water-soluble synthetic polymer with CH, CH_2 and OH as side group. It is non-toxic, has high tensile strength and flexibility. Polyvinylpyrrolidone is soluble in water and other polar solvents. It is initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production. The imide group (N–C=O) in PVP exists in the collagen molecular structure too. But, the influence of the functional group in collagen on inorganic crystal is difficult to study due to the complicated structure of protein. This leads to the use of PVP as a replacer [26]. They were employed to prepare a composite using a biomimetic approach with mild solution conditions (less than 100 °C) for the synthesis of HA nanopowder. Obtained results were then compared to pure nano-HA elaborated by wet chemical precipitation. We reported here their effect on the thermal behavior, phase formed, size, morphology and the obtained phosphocalcic ratio. The surface-regulating polymers PVA and PVP are used as capping agent to regulate the nucleation and crystal growth of HA crystal.

2. Experimental

2.1. Materials

In situ preparation of hydroxyapatite nanoparticles was carried out in the presence of two different types of polymers (PVA and PVP) named HAV and HAP, respectively, as the flow chart described in Fig. 1. For comparison HA nanoparticles were prepared by wet chemical precipitation method in the absence of polymer named SHA [27].

In order to study the effect of types of polymer on the preparation of nanohydroxyapatite, polyvinyl alcohol (PVA) (Loba Chemicals, India) and polyvinylpyrrolidone (Winlab, UK) were chosen. The first step in the preparation of HA nanoparticles was the preparation of a 1.388 M calcium chloride dihydrate (AR) (Sisco Research Laboratories, India) solution and a 0.833 M solution of di-ammonium hydrogen phosphate (LR) (Arabian Medical & Scientific Lab. Sup. Co., UAE). The two solutions prepared separately.

The calcium chloride dihydrate stock solution was slowly added to the polymer solution with a continuous stirring and heating for approximately 10 min. The pH of the solution was adjusted to 11 by sodium hydroxide. After stirring, di-ammonium hydrogen phosphate solution was added gradually to the above mixture. A milky white coloration was observed almost instantaneously after the addition of phosphate solution. The pH of the solution was adjusted to 11 again. The temperature was risen to 90 °C with constant stirring for 2 h. High values of pH in the solution have been reported to promote HA nucleation through the following reaction [14]:

$$5Ca^{2+} + 3PO_4{}^{3-} + OH^- = Ca_5(PO_4)_3OH$$

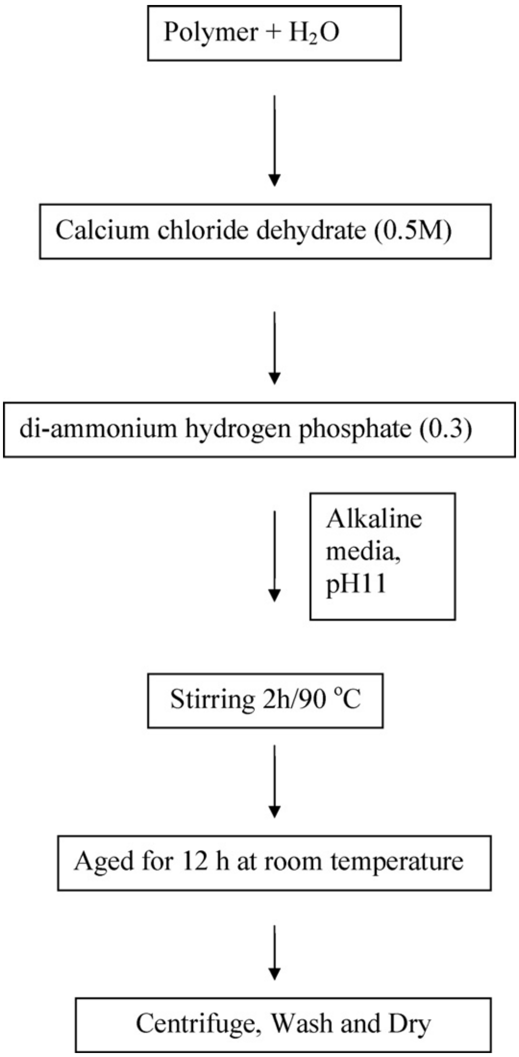

Fig. 1. In situ synthesis of nanohydroxyapatite in polymeric matrix.

The solutions obtained in this manner (with polymer) (HAV and HAP) and that without polymer (SHA) were centrifuged at 4500 rpm for 30 min and washed with distilled water then dried in an oven at 60 °C over night.

2.2. Characterization

The thermal behavior of the as-dried prepared powder samples (SHA, HAV and HAP) was characterized by using differential thermal analyzer Labsys 1600. Phase composition of the powders was determined by the X-ray diffraction method in the range of 2θ from 20 to 90 using (Inel Diffractometer) with Cu Kα radiation. Then the morphology of the powders was studied using scanning electron microscope (SEM) (JEOL JSM 6301f). Surface area measurements (BET) were determined by using NOVA 2000 USA and the crystallite size was calculated. Inductively coupled plasma-optical emission spectrometer (ICP-OES), type CIROS Vision was used to determine the ionic concentration of the prepared powders and the calcium to phosphorous molar ratio. Elemental analysis (EDS) (Oxford Link INCA) was also used in the goal to characterize the ions present too.