Development of hydroxyapatite/polyvinyl alcohol bionanocomposite for prosthesis implants

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Abstract. Hydroxyapatite (Ca10(PO4)6(OH)2) has similar structural and chemical properties of natural bone mineral and hence widely used as a bone replacement substitute. Natural bone consists of hydroxyapatite and collagen. For mimicking the natural, in the present work, a sintered porous hydroxyapatite component has been vacuum impregnated with Polyvinyl alcohol (PVA), which has better properties like biocompatibility, biodegradability and water-solubility. Hydroxyapatite powders have been made into nanosize to reduce the melting point and hence the sintering temperature. In the present investigation high energy ball mill is used to produce nano-hydroxyapatite powders in bulk quantity by optimizing the milling parameters using stainless steel grinding media. Pellets of 10 mm diameter have been produced from nano-hydroxyapatite powders under different uniaxial compaction pressures. The pellets have been sintered to form porous compacts. The vacuum impregnation of sintered pallets with PVA solution of different strength has been done to find the optimum impregnation condition. Microhardness, compressive strength, wear loss and haemocompatibility of hydroxyapatite ceramics have been studied before and after impregnation of PVA. The nano-hydroxyapatite/PVA composites have superior mechanical properties and reduced wear loss than the non-impregnated porous nano-hydroxyapatite ceramics.

Keywords: Bionanocomposite, nano-hydroxyapatite, prosthesis implants, haemocompatibility, polyvinyl alcohol.

1. Introduction

Prosthesis implants are used to replace the injured part of the human body. Bone implants play the role of natural bone’s functions in our body, so the properties such as composition, structure, strength, fracture toughness and other properties should match the properties of natural bone. To mimic natural bone with prosthesis implants we should clearly know the bone’s hierarchical structure and composition. Bone mainly consists of collagen fibres and an inorganic bone mineral in the form of...
small crystals. Dry bone consists of approximately 60-70% of bone mineral, 30-40% of collagen, and the remaining 2-5% of other substances such as proteins and inorganic salts. The composition of the mineral component can be approximated to hydroxyapatite (HA), which has the chemical formula Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. However, it is not exactly HA but it is an approximation since hydroxyapatite has a Ca:P ratio of 5:3 (1.66), whereas bone mineral actually has a Ca:P ratio ranging from 1.37-1.87 and has internal crystal disorder. The other main constituent in the bone is the collagen. It has a triple helical structure, and specific points along the collagen fibres serve as nucleation sites for the bone mineral crystals [1].

The human body is not an easy environment for a material to function in for prolonged periods. It must be able to operate for many years at a temperature of 37°C in a very moist environment. Also, bone growth can only occur in acidic conditions as these are necessary for mineral deposition, so the implant must be capable of withstanding this for many years without corroding. Implant materials must be designed to minimize the adverse reactions associated with introducing a foreign material to the body. The materials used in each component of the prosthesis implant must have suitable properties to allow them to replace the natural tissue and continue to perform the same functions. HA is the main mineral constituent of teeth and bones. HA ceramics does not exhibit any cytotoxic effects. It shows excellent biocompatibility with hard tissues and also with skin and muscle tissues [2]. HA is not only bioactive but also osteoconductive, nontoxic, nonimmunogenic, and its structure is crystallographically similar to that of bone mineral [3]. The flexural strength, strain-to-failure, and fracture toughness values of HA-ceramics are significantly less than those of bone, whereas the elastic modulus is much higher. To improve the mechanical compatibility of HA ceramics, the composite approach can be successfully adopted. The polymer-HA composites can be successfully used in most of the clinical applications. Polyvinyl Alcohol (PVA) is widely used in pharmaceutical, biomedical and biochemical applications due to its many desirable characteristics, such as biocompatibility, biodegradability, and water-solubility [4][5]. The objective of the present work is to develop a hydroxyapatite (HA)/polyvinyl alcohol (PVA) bio-nano-composite for prosthesis implant by impregnation of polyvinyl alcohol solution into the open pores of the sintered implant produced from nano-hydroxyapatite powders.

2. Materials and Methods

Nano-HA powders for bio-implants have been produced successfully in bulk quantity using high energy planetary ball mill from the micron-sized HA powders. The ball to powder weight ratio (BPR) of 10:1 and 15 h milling were optimum for producing nanostructured HA (crystallite size ~120 nm) with low contamination level using stainless steel grinding media. Unmilled (micron-sized) and milled (nano-sized) HA powders have been compacted under uniaxial compaction pressures of 50-250 MPa and sintered to form porous 10 mm dia pellets. Sintering at 950°C for 2 h in normal air atmosphere was optimum for producing 30-40% of open porosity which was found to be good for PVA impregnation. The 4% PVA solution is found to impregnate the porous ceramics effectively during the vacuum impregnation process to form nano-HA/PVA composite. Microhardness of the pellets has been obtained using Vickers microhardness tester (UHL VMHT). 300 g load has been applied for 10 s to make the indentation on the samples. The pellets have been tested in UTM (Tinius Olsen model H50K-S) for their compressive strength. The standard pin-on-disc apparatus (Ducom, India TR-20) with a surgical grade stainless steel disc of 230 mm diameter has been used for wear tests. The carboxymethyl cellulose solution (1 gram in 100 ml of distilled water) has been used as lubricant while testing, because of its similarity of rheological properties with synovial fluid. The wear tests have been carried out for 20 minutes at sliding velocity of 0.24 m/s under the load of 10 N [6]. The haemolysis count is one of the important parameter in testing the biocompatibility of materials. Haemolysis indicates premature destruction of red blood cells when they come in contact with water or other foreign elements. The haemolysis counts of the developed composites have been obtained with the help of goat’s blood. The haemolysis count test procedure can be found elsewhere [7].
3. Results and Discussion

The XRD patterns of HA powders milled at different time intervals with 10:1 BPR has been shown in Figure 1. XRD pattern of unmilled sample (0 h) is compared with XRD patterns of milled samples. It shows continuous peak broadening with increasing milling time, which indicates the refinement of hydroxyapatite powder. The extra peaks are from some new phases such as Fe$_3$(PO$_4$)$_2$ and FePO$_4$, which are formed during milling due to wear of grinding balls and vials. It indicates the contamination in the starting material due to milling. Figure 2 shows the photograph of sintered pellets prepared from nano-hydroxyapatite powders under different uniaxial compaction pressure (50MPa, 100MPa, 150MPa, 200MPa and 250MPa). Higher compaction pressure increases the bulk density and mechanical properties, whereas the amount of porosity in the pellets decreases.

Nano-hydroxyapatite pellets have been sintered at 950°C for 2 h to achieve 30–40 % of open porosity. The change in the open porosity percentage with compaction pressure has been shown in Figure 3. Total amount of open porosity in the nano-hydroxyapatite pellets decrease with increasing compaction pressure. Microhardness of the pellets increases with increasing compaction pressure (Figure 4). The variation of the compressive strength of the nano-HA pellets and nano-HA/PVA composite with compaction pressure is shown in Figure 5.

![Figure 1. XRD patterns of as-milled hydroxyapatite powder (BPR 10:1)](image1)

![Figure 2. Photograph of nano-HA pellets after sintering (Sintering temp: 950°C, sintering time: 2h, compaction pressure: 50MPa to 250MPa from left to right)](image2)

Compressive strength increases with increasing compaction pressure. The compressive strength of the nano-HA pellets ranges from 105 – 119 MPa. Composite of nano-HA and PVA has compressive strength of 140 – 163 MPa, which depends on the compaction pressure.
Figure 3. Open porosity Vs. Compaction pressure plot for nano-hydroxyapatite pellets

Figure 4. Effect of compaction pressure on microhardness values of nano-HA pellets

Figure 5. Variation in compressive strength of porous nano-HA ceramics and nano-HA/PVA composites with compaction pressure

Higher compaction pressure produces denser pellet and thereby increases the hardness and strength. Higher compaction pressure gives more densification in the pellets, leads to reduced porosity. The high porosity in the pellet produced at lower compaction pressure cause earlier fracture and lead to low compressive strength. Polyvinyl alcohol impregnation in the nano-HA pellets has been found to improve its compressive strength (Figure 5).
The wear loss decreases with increasing compaction pressures (Figure 6). The polyvinyl alcohol impregnation into the ceramic matrix improves the wear resistance of the pellet. The wear volume has been found comparatively low for nano-hydroxyapatite/PVA composite when compared to pure nano-hydroxyapatite pellets. The pellet produced with higher compaction pressure gives low porosity and high strength, therefore the wear loss is very low. The impregnated PVA reduces the wear of hydroxyapatite.

![Figure 6](image1.png)

**Figure 6.** Wear volume Vs Compaction pressure plots for nano-HA pellets and nano-HA/PVA composite

Haemocompatibility is the compatibility of the material with the blood. The haemolysis percentage has been calculated for starting materials and final product using goat’s blood. The haemolysis percentages for starting materials (PVA and nano-HA powder) and products (porous nano-HA pellets and nano-HA/PVA composite) have been shown in Figure 7.

![Figure 7](image2.png)

**Figure 7.** Haemolysis percentage (%) of starting materials and products

The accepted norm is that if the haemolysis percentage is less than 10 the test material is taken as haemocompatible and if it is less than 5 the material is highly haemocompatible (Roy Chowdhury et al. 2007). The composite has haemolysis percentage of ~3 % and is well below 5 so it is a highly haemocompatible material.
4. Conclusions

- Nano-hydroxyapatite powders for bio-implants have been produced successfully in bulk quantity using high energy planetary ball mill.
- Nano-HA powders have been compacted under uniaxial compaction pressures of 50-250 MPa and sintered to form porous compacts. The mechanical properties and wear resistance of the porous compacts increased with compaction pressure.
- Sintering at 950˚C for 2 h in normal air atmosphere was optimum for producing 30-40% of open porosity which was found to be good for PVA impregnation.
- The 4% PVA solution is found to impregnate the porous ceramics effectively to form nano-HA/PVA composite.
- PVA impregnation improved the microhardness and compressive strength of porous nano-HA ceramics and reduced the wear loss.
- Sintered nano-HA ceramics with or without PVA impregnation have manifested excellent haemocompatibility.

5. References

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