

Synthesis and Characterization of Nano Hydroxyapatite with Polyoxymethylene Nanocomposites for Bone Growth Studies

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Abstract: *The hydroxyapatite which is incorporated with organic polymer for the formation of nano composite material is used biomedical engineering. According to prior researches its chemical similarity to bone and dental, this product could improve bioactivity and bonding ability of bone formation. Hap is one among the few bioactive materials that will support bone in orthopedic, dental and maxillofacial applications. In this research, nano hydroxyapatite/polyoxymethylene composite material was prepared by wet chemical precipitation method. The chemical characterization on the nano composite was evaluated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Transmission electron microscopy (TEM) and thermal analysis TG/DTA. The sizes of the nano composites were confirmed by the TEM and XRD studies.*

Keywords: FTIR, XRD, TEM, TG/DTA and POM

1. Introduction

Synthetic hydroxyapatite is a bioactive material that is chemically compatible with biological apatite. The mineral constituents of hard human tissues such as bones and teeth have similarity with synthetic hydroxyapatite¹⁻³. With excellent biocompatibility and bioactivity, hydroxyapatite has been widely used in medical, dental and other health-related field as material for damaged bones or teeth. They can be used as implant, scaffold materials and as drug delivery agents⁴⁻⁵. HAp plays a keyrole in the field of orthopedic and dental because of its appreciable host responses in the biological environment. The chemical, structural and morphological properties of synthetic HAp can be modulated by varying the method and the conditions of synthesis. Classical methods for HAp powder synthesis include direct wet chemical precipitation, hydrothermal techniques, hydrolysis of calcium phosphate as well as solid state reactions⁶⁻⁷ and mechano-chemical methods. One of the most widely used methods is wet chemical precipitation, where chemical reactions take place between calcium and phosphorus under a controlled PH and temperature. Several biodegradable materials have been investigated as carriers for bone growth factors, including organic materials⁸, such as inactive demineralized bone proteins⁹⁻¹⁰ ceramics,¹¹⁻¹² and synthetic polymers such as polylactide and polylactide-polyglycolide co-polymer. Possible clinical applications for bone growth factors include impaired bone healing, inadequate bone stock, and incomplete incorporation of prosthetic implants into bone.

Reconstruction of bone with fully synthetic artificial bone graft is another way to provide and create lost bone mineral. Calcium phosphate is highly promising as a bone substitute in orthopedics among the other ceramics¹³. Biodegradable polymers offer a number of advantages for developing bone at defect sites¹⁴ and biodegradable polymers can be used to impart macroporosity to cement as polymers degrade and expose macropores to grow its structure. In bone application, biodegradable polymer or

its composite can be prepared in two forms, one is scaffold and another one is dense. Usually scaffold is used to associate with cell seeded in purpose of cell growth to form bone. Dense form of biodegradable polymer can be obtained from forging, hot or cold processing¹⁶.

2. Materials and Methods

Materials

The entire chemical was synthesized through a high frequency microwave accelerated with wet chemical precipitation method. The raw materials required to start the processing of the composite were: analytical grade calcium hydroxide, ammonium dihydrogen phosphate. They were purchased from Sigma Aldrich and polyoxymethylene was procured from Alfa Aesar. Hot water, ethanol and doubly distilled water were used as the solvent.

Methods

Synthesis of hydroxyapatite

In this method two different chemical reagents (precursors) were used. At first calcium hydroxide solution was slowly added to a solution of ammonium dihydrogen phosphate and after proper mixing, these reagents in aqueous medium with a PH of 11 were immediately subjected to high frequency microwave irradiation for about 20 min. The precipitate was washed with distilled water to remove impurity ions (NH₄⁺). The product obtained after filtration was oven-dried at 90°C.

Synthesis of Hydroxyapatite with Polyoxymethylene

The HAp/POM nano composites were coded as nHAp/POM (80-20), nHAp/POM (70-30), nHAp (60-40) where number denotes the wt. % used in the processing. Hot water was used as the solvent to prepare the polymer solution. Polyoxymethylene was dissolved by using

magnetic stirrer for 2h. Then suitable amount of nHAp was added to polymer solution. The homogeneously mixed solution is immediately taken to microwave oven. The resultant HAp/POM nano composite powder was thoroughly mixed using a mortar and pestle for 20 min.

3. Results and Discussion

The FTIR spectra of pure HAp/POM with different wt. % of nano composites are shown in figure 1. The FTIR spectrum investigation was carried out using Perkin Elmer spectrometer in the range of 400 - 4000 cm^{-1} . The bands 3420, 3416 and 3409 cm^{-1} (Kannan and Ferreria 2006), while the band 1661 cm^{-1} overlap the -OH groups. Similarly, the observed bands at 1463, 869 and 818 cm^{-1} are assigned to carbonate ions (Pan and Xiong 2009; Paulo et al.2011; Pramaxnik et al, 2006, 2008). The bands at 2830 and 2958 cm^{-1} are assigned to the hydroxyl groups present in POM. The characteristic bands of POM absorption are observed at 2952, 2729, 1463, 1376, 1377, 1248 and 1035 cm^{-1} . The bonds located at 1036 cm^{-1} is attributed to the PO_4^{3-} groups. The observed bands at 601-603 cm^{-1} are due to phosphate bending vibration. The phosphate stretching mode appeared at 564 -566 cm^{-1} corresponds to PO_4^{3-} groups.

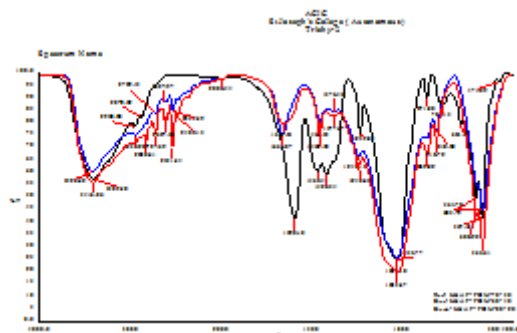
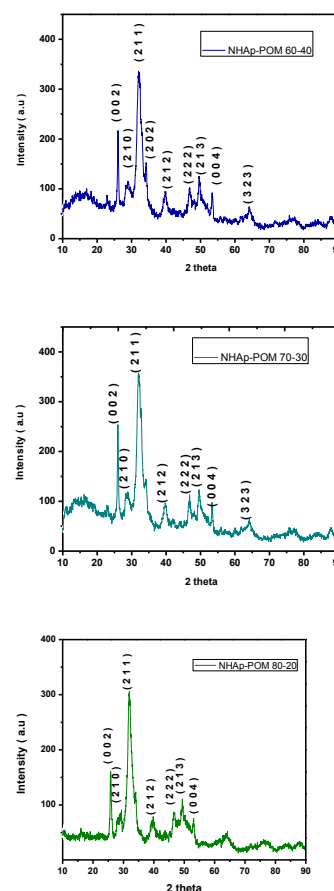


Figure 1: FTIR spectrum of HAp with POM different wt % of nanocomposites

XRD

The XRD patterns of nano HAp with POM composites were taken. The pattern indicate the presence of crystalline HAp. The reflection plans corresponding to the characteristic XRD spectral peaks of pure nano HAp and POM composites are shown in Fig.2. The XRD pattern for the HAp/POM in different weight composites indicating the stability of POM matrix. In The XRD patterns, diffraction peaks have been identified as hexagonal phase of HAp powder (JCPDS card no: 09-0432). Crystalline size and crystallinity of hydroxyapatite were investigated with powder XRD spectrum and broaden diffraction peaks at $2\theta = 25.8, 32.0, 39.0$ and 47.0 respectively. These phases are assigned to the Miller's Indices reflection planes (002), (211), (212) and (222). This indicates that the amorphous phase of HAp and crystallite size is very small ranging from 20 nm to 100 nm. This XRD spectrum indicates most of the high intensity peaks positioned between $2\theta = 25^\circ - 47^\circ$ and we observed that a peak

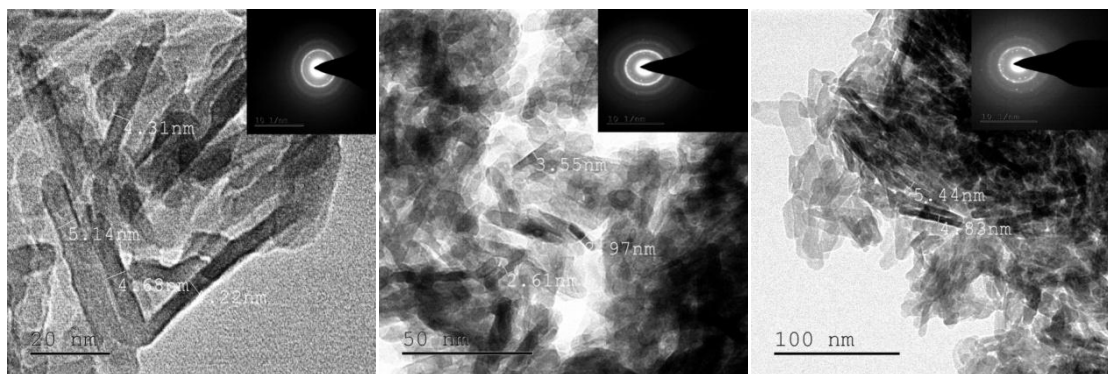
broadening is due to the presence of HAp crystallite with a size of nano scale.



(a) 60-40 % (b) 70-30 % (c) 80-20 %
Figure 2 (a), (b) and (c) XRD of HAp/POM Nanocomposite

TEM

The structure and morphology of the samples were further confirmed by the TEM images (fig.3) of the prepared nano hydroxyapatite with polymer composites. In order to confirm the XRD results concerning the presence of HAp crystallites in the composite samples, TEM measurements were performed. The TEM micrographs, revealed the structural features of the composites. The nHAp/ polymer with different weight % of the sample (Fig.3) reveal the existence of nano crystallites ranging 20 nm to 100 nm length and 2 nm to 5 nm width, while TEM image associated these nano crystallites with the presence of HAp, through Miller indices (hkl) confirming the XRD results. The particles size is also found to be in agreement with previous report Ferraz et.al. (2004). In addition the selected area electron diffraction (SAED) of the precipitates shows diffraction ring of patterns, which implies that the precipitates are crystalline nature. This is agreed with XRD results.



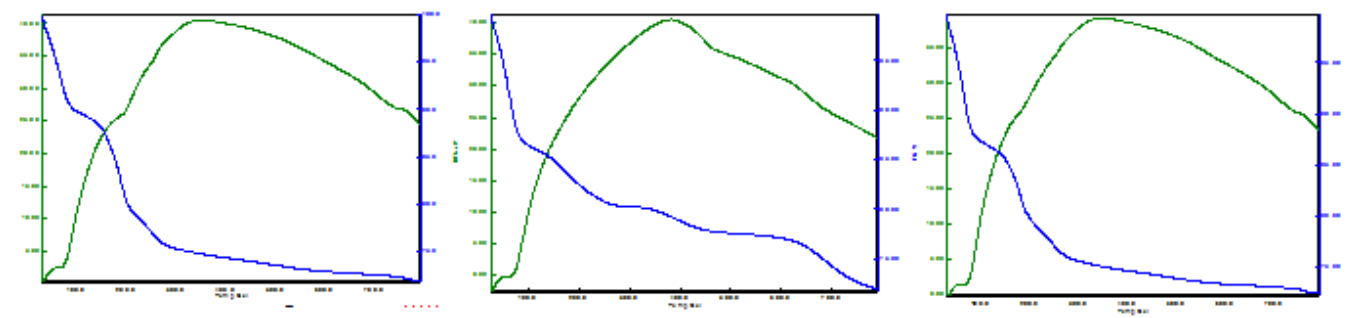
(a) 80-20 % (b) 70-30% (c) 60-40%

Figure 3 (a), (b), (c) TEM and Selected Area Electron Diffraction (SAED) images of HAp/POM nanocomposite

TG-DTA

To evaluate thermal stability of nHAp-POM in different weight % of composites, TGA was performed on Perkin Elmer instrument in the temperature range 30 - 800°C in nitrogen atmosphere at a heating rate of 25°C min⁻¹. The sample weights were in the range of 5.428 mg. In the TGA curves several steps are observed. The first step, showing a small decrease in weight is associated with adsorbed water-removing when heated above 90°C. The second step from 280°C may be due to the dehydration reaction of organic residues in POM chains. This temperature shift to a higher temperature, when the nano HAp content

increases. The third step was degradation of POM matrix releasing CO₂ gas. This temperature shifts to a lower temperature in the TG curves in caused by the increasing nano HAp content. The fact that the second step is initiated at slightly higher temperature and third step occurs at slightly lower temperature than in pure POM is suggestive of the presence of chemical interaction between polymer and nano HAp. In the DTA curve a sharp exothermic peak is located at 450°C. There are two peaks at 380 °C , 50 °C for the derivative of the weight loss. The presented peaks are close to that observed for DTA analysis and are illustrated in fig.4.



(a) 80-20% (b) 70-30% (c) 60-40 %

Figure 4 (a), (b) and (c) TG-DTA analysis of synthesized HAp/POM Nano composite

4. Conclusion

The hydroxyapatite with polymer nano particle was confirmed by X-ray diffraction (XRD) and functional groups of the compound are identified using Fourier Transforms Infrared spectroscopy (FTIR). The structure and morphology of the sample were characterized using by Transmission Electron Microscopy (TEM) analysis confirms the presence of nHAp/POM nano particles with the particle size of around 20 nm to 100 nm. Thermal analysis was carried out using TG-DTA. Therefore it can be concluded that HAp based polymer materials are certainly among the most promising challenges in bioactive ceramic for the near future and consequently the research effort put in their development will continue to increase.

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