

Synthesis and Characterization of Nano Hydroxyapatite with Poly Propylene Glycol Nanocomposite using for Bone Cement

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Abstract:- Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$) powder have been successfully synthesized by a wet chemical precipitation method in the presence of poly propylene glycol(PPG). The synthetic nHAp/polymer nano composite have been used some medical application such as bone repair, bone augmentation as well as coating of implants or acting as fillers in bone (or) teeth. The model scaffold used in this study poly propylene glycol appeared to provide an osteoconductivity pathway by with bone will grow in factor. In this work, poly propylene glycol/ hydroxyapatite nano composite were analyzed and confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) and TG/DTA.

Keywords: XRD, FTIR, TEM, TG/DTA

INTRODUCTION

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ is chemically similar to the mineral component of bone and teeth. HAp is among the few bioactive materials meaning that it will support ingrowths and osteointegration when used in orthopedic, dental and maxillofacial applications [1, 2, 3]. Bone defect, ranging from small voids to large segmental defects are a prevalent and persistent problem in clinical orthopedics and dentistry. Bone defects arise from a variety of causes including fracture nonunion [4,5], dental and orthopedic implant fixation [6], trauma or tumour resection [7,8]. Current standard procedures for bone defect repair include autograft and allograft [9,10]. Autograft such as those derived from aspirated bone marrow, cancellous or cortical bone or vascularized graft are osteogenic, osteoconductive, osteoinductivity and are considered the gold standard [11,12]. On the other hand allografts are subject to cleaning and preparation process designed to remove cells to minimize immune response. Currently, several calcium phosphate are being often used, such as hydroxyapatite (HAp), tricalcium phosphate (α and β -TCP) and dicalcium phosphate (BCP). However, since HAp is only one stable at physiological conditions; it is the most commonly used for medical applications [13]. Nano hydroxyapatite is usually synthesized by the wet chemical precipitation method. Several methods are available for synthesizing HAp based nano structured materials like co-precipitation, sol-gel, reverse micromulsion, hydrothermal, microwave-hydrothermal, solid state reaction [14]. The latter one is the

most often used process, as it is a simple, low cast, and suitable method for medical applications.

Polymers have been used increasingly in a wide range of applications, particularly in the medical device industry. Poly propylene glycol has many properties in common with poly ethylene glycol. An extensive study has been made on natural collagen, gelatin, silk fibroin and synthetic poly ethylene, polyamide, polystyrene, poly (vinyl alcohol), poly (ethylene glycol) and poly (ether ether ketone) polymer to overcome the mechanical problems associated with bioceramics in bone tissue engineering applications [15-18]. Synthetic polymers are highly useful in biomedical field since their properties (e.g. porosity, degradation time and mechanical characteristics) can be tailored for specific applications. There are two types of bone, compact or coral and cancellous or trabecular (spongy) bone. They are several ways to improve the bioactivity of polymers for use of bone repair, such as compounding with bioactive inorganic particles, grafting with bioactive groups and forming bioactive coating. In a previous study, our research group developed a nano HAp/PPG composite by a co-precipitation method for bone repair and reconstruction. The composite exhibits good biocompatibility, osteogenesis and strong bonding between nHAp/PPG matrixes. Polymer was supporting a bone plays an important role in the movement, support and protection of virtual organs. However, it is susceptible to fracture as a result of physiological resorption, dental losses, trauma injuries, bone pathology, infection, aging, population and bone disease [19-21]. The ways of bone repair improve year by year, parallel to the development of high techniques.

EXPERIMENTAL DESIGN

Materials

All chemicals used were of analytical grade. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were obtained from Merck (India) and poly propylene glycol (mol.wt 1000) was purchased from Alfa Aesar. Deionized water was used as the solvent.

METHODS

Synthesis of nano HAp

Hydroxyapatite nanoparticles were synthesized by the wet chemical precipitation method. 7.48g of $\text{Ca}(\text{OH})_2$ was first dissolved in 100 ml of ethanol- water mixture (50:50%, V/V) and was stirred for 3 hours. A solution of 6.7g of $(\text{NH}_4)_2\text{PO}_4$ was dissolved in 100 ml volume of deionized water and then added to the $(\text{Ca}(\text{OH})_2)$ solution over the period of 24 hours. The precipitate was thoroughly washed with distilled water to remove impurity ions (NH_4^+). The pH of the slurry was measured digitally during the precipitation reaction, reaching a final value of pH 11.

Synthesis of PPG/ HAp nanocomposites

The PPG/HAp nanocomposite was synthesized by wet chemical precipitation method. Water was used as solvent to prepare polymer solution. PPG was dissolved by using magnetic stirrer for 3 hours. Then suitable amount of PPG solution was mixed with HAp solution under agitation. Then HAp/PPG nanocomposites were coded as HAp-80/PPG-20 where number denotes the wt%, where immediately subjected to 10 minutes in a microwave oven.

XRD RESULTS

The XRD spectra of the different calculating HAp powders studied are shown in fig.1. The spectra found are typically in agreement with those published in literature; all XRD spectra obtained have characteristics peaks consistent with the international centre for diffraction (JCPDS 2001) files for calcium phosphate. The predominant HAp phase was confirmed with JCPDS file no. 09-432. Crystallite size and crystallinity of hydroxyapatite were investigated with powder XRD spectrum and broaden diffraction peaks are $2\theta=26, 32, 33.5, 40$ and that are assigned to the Miller's indices reflection planes (200), (211), (300) and (200) respectively indicate. If it calculated from the broadening of peaks that the particle size of HAp crystalline size vary from 50nm-100nm. This XRD spectrum indicates most of the high intensity peaks positioned between $2\theta = 26-40^\circ$. We observed from the peaks are broadening, that the synthesized HAp crystallite size present in nano scale level.

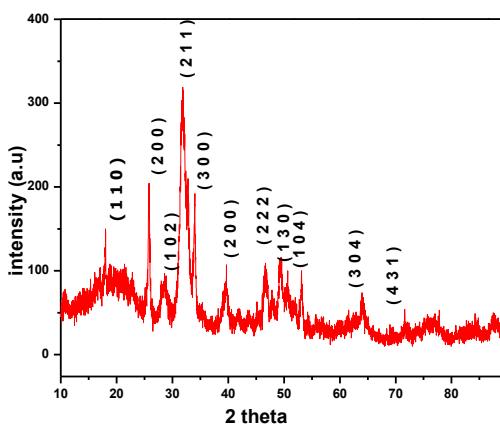


Fig.1. XRD Pattern of Nano HAp-80% with PPG-20% FTIR

The FTIR was used to study the effect of the substitution of the different functional groups, such as hydroxyl and phosphate groups of hydroxyapatite. FTIR spectra of HAp/PPG are recorded in the spectral region 4000-400 cm^{-1} and represented in fig.2. An absorption at 3429.47 cm^{-1} indicate the presence of alcohol O-H group. The strong band CH_2 was detected in the region around 2973.79 and 2874.97 cm^{-1} in sample which confirms the presence of polymer substitution. The medium peak 1402.59 cm^{-1} indicates or confirms the mineral amount of carbonate substitution. The band 1258.42 cm^{-1} indicates the presence of aliphatic amines. The strong peak CO_3^{2-} groups at 862.18 and 1579.57 cm^{-1} indicate that the HAp powder is particularly carbonated hydroxyapatite, as commonly observed in organic reagent. The band at 608 and 566 cm^{-1} are due to phosphate bending vibration. From these measurements, the precipitate particle is proved to be HAp with PPG.

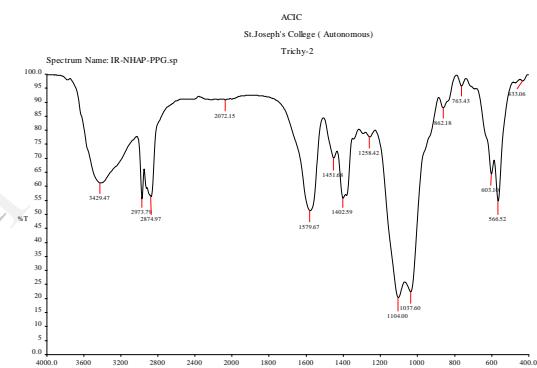
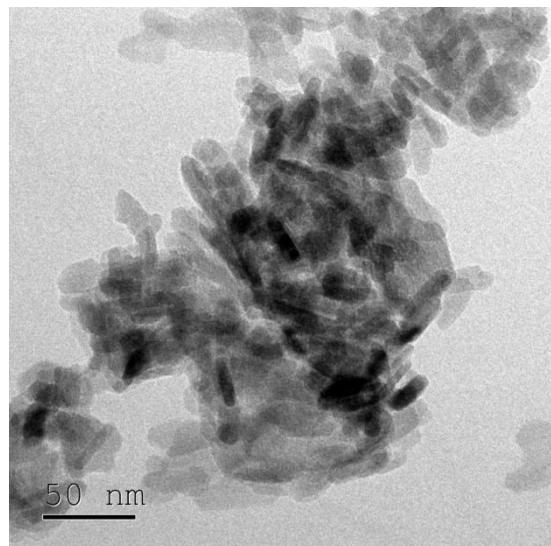


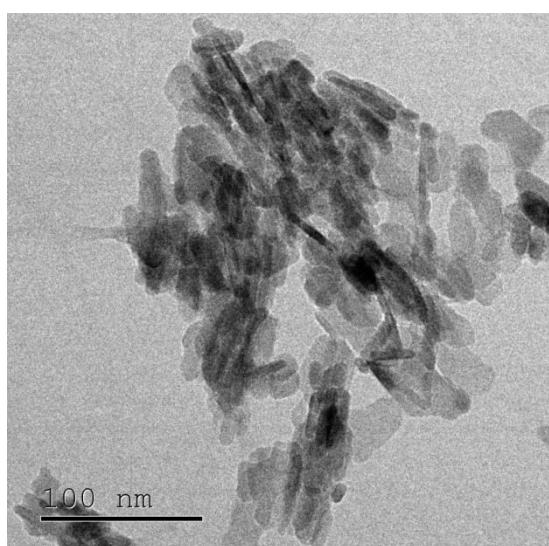
Fig.2 FTIR Spectrum of nanoHAp -80% With PPG-20%

TEM

The transmission electron microscopy (TEM) has been found to be an excellent tool for characterizing the size of nano particles. The structure and morphology of the sample were further confirmed by the TEM images of the prepared nano-hydroxyapatite as shown in fig. (3). The transmission electron microscopic analysis confirms the presence of the rod-like morphology of the prepared HAp nano particle with the particle size of around 50 to 100 nm. The particle size is also found to be in agreement with the report results of Ferraz et al. (2004). In this work, organic solvent was used to replace the water in the system because it can decrease the two major factors that cause the agglomeration of nano powder when drying from aqueous solutions: one is the capillary pressure between the adjacent particles due to evaporation of water and the other is the hydrogen bond originating from the water molecules on the surface of adjacent particles. The inserts are their corresponding selected area electron diffraction (SAED) patterns. The diffraction dots or rings reflected crystallinity of samples. The SAED results of nano HAp with PPG are in good agreement with the lattice structure of hydroxyapatite and exhibit excellent crystallinity.

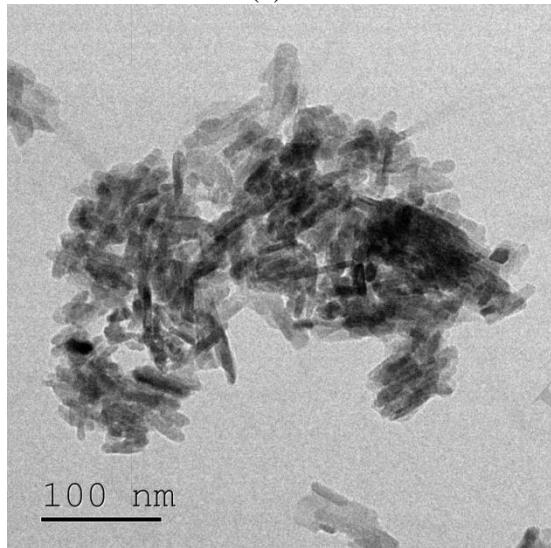


(a)

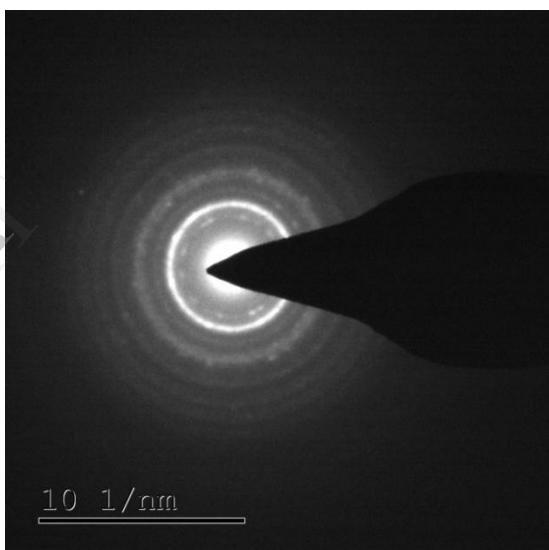


(c)

Fig. 3 (a), (b) and (c) TEM image of NHAp-80% with PPG-20%



(b)



(d)

Fig. Image 3(D) selected area electron diffraction (SAED) patterns of NHAp with PPG.

TGA/DTA

TGA/DTA tell the physical properties of the polymer used in the scaffold preparation. TGA shows the change in mass with increase of temperature. TGA/DTA studies have been carried out on HAp-PPG composite sample in 80-20 % of weight. Using Experiments PYRIS 7 TGA analyzer, Perkin Elemer Inc., US., have been performed using simultaneous TGA/DTA analysis by heating the sample at 30 cel/min in the temperature range 30 $^{\circ}$ C and 900 $^{\circ}$ C in the nitrogen atmosphere and a typical plots has been shown in figure (4). The curve in color Blue stands for the TGA while the another color green stand for DTA. TGA shows the 1.4% initial loss due to moisture. The first onset temperature, 2nd onset temperature, first 10% degradation temperature, 2nd 10% degradation temperature first maximum slope, 2nd maximum slope are 120 $^{\circ}$ C, 400 $^{\circ}$ C, 850 $^{\circ}$ C respectively. The total degradation temperature

loss is 42.7%. DTA curve shows endothermic peaks at 450 °C are due to thermal degradation. There is two step degradation, the initial degradation is due to moisture and 2nd degradation is due to composite.

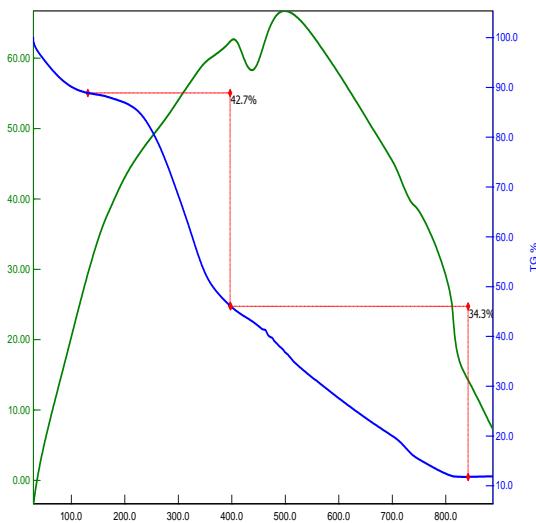


Fig.4 TGA/DTA curve of NHAp-80% with PPG-20%

CONCLUSION

The development of bone tissue engineering scaffolds based on polymer with hydroxyapatite nano composite was analyzed experimentally. In bone tissue engineering, HAp/PPG are used as filling material for bone defects, augmentation, artificial bone graft material, prosthesis revision surgery. Its high surface area leads to excellent osteoconductivity and restorability favorable for fast bone. The experimental results of this study show that this large pored hydroxyapatite material has high strength and density very close range to that of actual femoral bone. The XRD pattern shows diffraction peaks with line broadening and high intensities, which confirms the nanosize with crystalline nature. The TEM image confirms the nano crystalline nature of synthesized powder and needlelike morphology of the particles. In addition, the particles showed less agglomeration. The selected area electron diffraction (SAED) studies showed that diffraction ring of patterns which implies that the ceramic particles are crystalline in nature, which is also proved by XRD results. The FTIR spectrum confirms the formation of HAp/PPG. The thermal stability is there up to 900 °C and minimum weight loss. The synthetic bone substitutes will probably be commercially available for orthopedic applications in the near future.

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