Synthesis and Characterization of Nano Hydroxyapatite with Polymer Matrix Nano Composite for Biomedical Applications

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Abstract: Hydroxyapatite is chemically similar to the mineral component of bone and teeth. A novel nano composite involving nHAp/polymer matrix has been successfully synthesized by wet chemical precipitation method at room temperature. The purpose to synthesize such nano composite is to respect to suitable biocompatibility, bioactivity, cytotoxicity and mechanical properties. The FTIR spectra of nHAp/polymer matrix indicated significant intermolecular interaction between the various vibrational modes corresponds to phosphate and hydroxyl groups. The results of XRD, TGA/DTA suggested that the crystallinity and thermal stability of the nHAp/ polymer matrix peaks have decreased and increased respectively. The size and morphology of the sample were characterized using Transmission Electron Microscopy (TEM).

Keywords: FTIR, XRD, TGA/DTA, TEM

1. Introduction

Hydroxyapatite (HAp) which has molecular stoichiometric formula ($Ca_{10}(PO_4)_6(OH)_2$), has been extensively investigated due to its excellent biocompatibility, bioactivity and osteoconductivtity as well as its similarities to the main mineral component of bone. However, it has been reported that HAp in the form of powders, used for the treatment of bone defect, has problems associated with migration to places other than implanted areas. Among them, hydroxyapatite is frequently used in orthopedic, dental and maxillofacial applications, meaning that it supports bone growth and osteointegration [1-3]. Recently, research on the functional bone substitutes such as apatite has been a major subject over the year [4]. Belonging to the family of apatite, nHAp has been widely used as artificial bone substitutes in biomedical applications because of its excellent bioaffinity, osteoinductivity and nanoproperties [5]. Several methods are available for synthesizing HAp based nano structured materials like co-precipitation, sol-gel, and reverse microemulsion, hydrothermal and solid state reaction [6]. Co-precipitation from a apatite polymer matrix aqueous solution is one of the effective and economic methods for nHAp preparation [7]. The microstructure and property of the resulting nHAp powder greatly depends on the properties of the polymer matrix. Hence, in recent years considerable attention has been focused towards the development of polymer composites to fulfill the requirement for biomedical applications.

Some excellent reviews have discussed the various types of degradable polymers and their co-polymers [8-14]. Therefore, this subject will not be discussed in detail in this review. The scope of this paper is to give a perspective of the facts that enter into bone tissue engineering using degradable polymers in particular. Recently, the characteristic of a degradable polymer to be respected prior to implantation have been divided into two main categories: biocompatibility and biofunctionality [15]. Biocompatibility refers to the aspects concerning the absence of toxicity, immunologenicity,

carcinogenicity and thrombogenicity [15]. Biofunctionality refers to the aspects of adequate properties (mechanical, physical, chemical, thermal and biological) easy to handle, sterilizable, storable and resorbable [15]. Various types of polymers have been combined with calcium phosphates (mainly hydroxyapatite) to prepare nano composites with improved biocompatible and mechanical properties [16-18]. Synthetic polymers were studied as potential matrices of composite materials with hydroxyapatite (HAp) for possible application as bone analogues: Polymethyl methacrylate and Poly vinyl pyrrolidone. Several studies have investigated the synthesis and characterization of hybrid materials based on HAp and biodegradable polymers.

2. Materials and Methods

2.1 Materials

The raw materials required to start the processing of the composite were: analytical grade Calcium hydroxide ($Ca(OH)_2$) was purchased from Sigma Aldrich and ammonium dihydrogen phosphate ($(NH_4)\ H_2PO_4$) procured from Mercy (Mumbai, India). Poly vinyl pyrrolidone (Mw 40000) was purchased from Sigma Aldrich and Poly methyl mathacrylae were purchased from Alfa Aesar. Doubly distilled water with ethanol was used as the solvent.

2.3 Methods

2.3.1 Synthesis of HAp/PMMA and PVP nano composites

The First calcium hydroxide was slowly added to a solution of ammonium dihydrogen phosphate and after proper mixing, the HAp was precipitated by adding ammonia and pH of the solution was maintained from 9 to 11. The solution was constantly stirrer for 24h by magnetic stirrer, allowing the reaction to complete. The resultant precipitate was separated and ammonia was removed by repeated washing. The precipitate was allowed to dry in an oven at 90 °C subsequently; aggregates formed were crushed into fine powder. In a separate study synthesized HAp powder (80) was mixed with polymer solution (20) where number denotes the wt% and the resultant HAp - PMMA and PVP composite powder was thoroughly mixed using a mortar and pestle for 30 min.

3. Result and Discussion

3.1 FTIR

The Prepared samples were studied by Fourier Transform Infrared Spectroscopy (FTIR) using Perkin Elmer spectrometer in the range of 400 cm^{-1} to 4000 cm^{-1}. The FTIR spectra of pure nHAp with PMMA and PVP composites are shown in figure1. The peak observed at 3142.93 cm^{-1} corresponds to the stretching mode of –OH group, which characterize the presence of calcium phosphate such as HAp. The characteristic band of PMMA, absorption of C=O, $-CH_2-$ appeared at 2791.56, 2364.02, 1462.74 and 875.62 cm^{-1} respectively. The bands located at 1034.18 cm^{-1} is attributed to the PO_4^{3-}. It is confirmed with the report presented (Urch et al 2009) at 1292.13 cm^{-1} and 1662.85 cm^{-1} confirms the presence of polymer (PVP). The observed bands at 602.59 cm^{-1} are due to phosphate stretching mode is appeared at 565.02

cm^{-1} corresponds to PO_4^{3-}group.

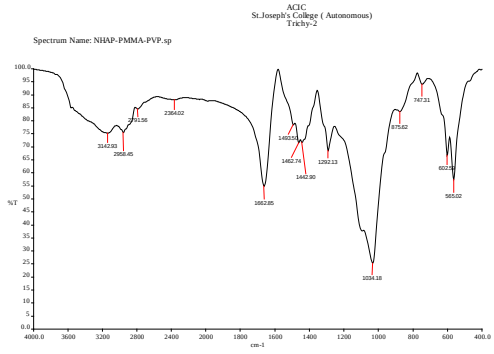


Fig.1. FTIR spectrum of nHAp with polymer matrix.

3.2 XRD

X-ray diffraction pattern, typical of the composites, is shown in fig (2). The strong peaks present in the XRD patterns were readily indexed with the nano composites shows the most intense peaks 211 and 212 at 2θ=31.5°, 38.5° attributed to HAp. Then polymer matrix peaks are observed at 202, 213. The broad peaks and very wide baseline in the powder pattern indicate that the structure has the inorganic component. The patterns were in good agreement with JCPDS (09-0432) and confirmed to the pure phase of HAp and polymer matrix. If it is calculated from the boarding of peaks that the particle size of HAp crystalline size is varied from length (20 nm to 100 nm) and width (2 nm to 4 nm).

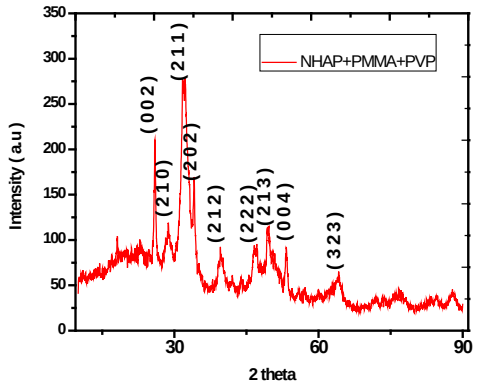
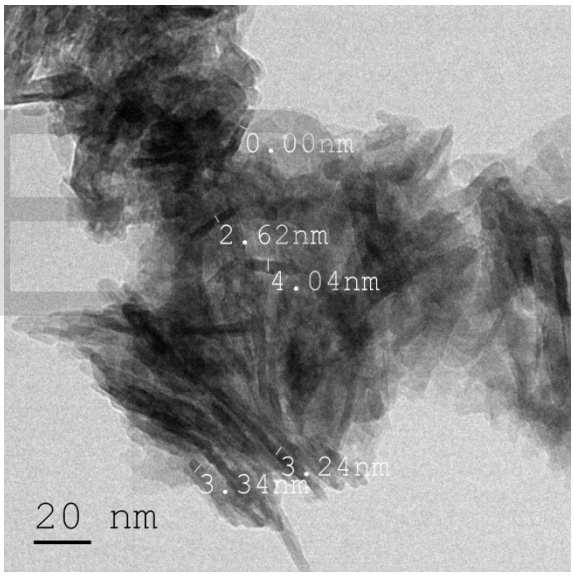


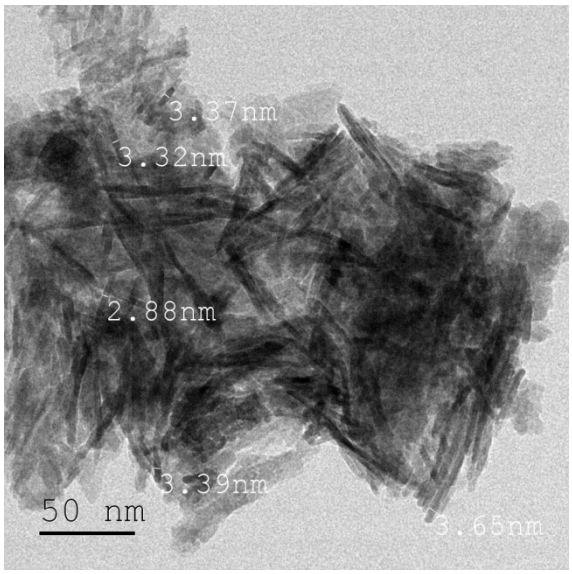
Fig.2. XRD of nHAp/ polymer matrix

3.3. TEM

The structure and morphology of the samples were further confirmed by the TEM images of the prepared hydroxyapatite with polymer matrix as shown in fig. (3). The micrographs reveal that synthesized HAp with polymer contains rod-like morphology of length varying from 20 to 100 nm and width varying from 2 to 4 nm. The particle size is also found to be in agreement with the report results of (Ferraz et al. 2004). From TEM images, the HAp is visible as dark contrast areas and seen uniformly dispersed throughout the polymer matrices. In addition, the selected area electron diffraction (SAED) of the precipitates shows that diffraction ring of patterns. It implies that the precipitates are crystalline in nature. This is in agreement with XRD results.

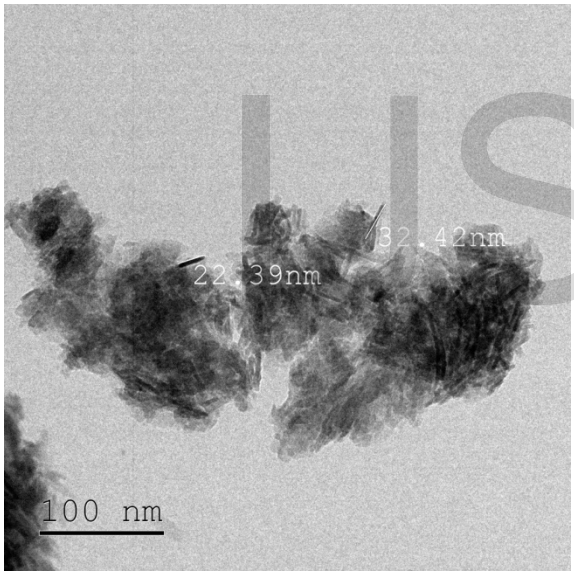


(a)



(b)

(d)



(c)

Fig.3 (a), (b), (c) TEM images and (d) Selected Area Electron Diffraction (SAED) image of nHAp/Polymer matrix.

3.4.TGA/DTA

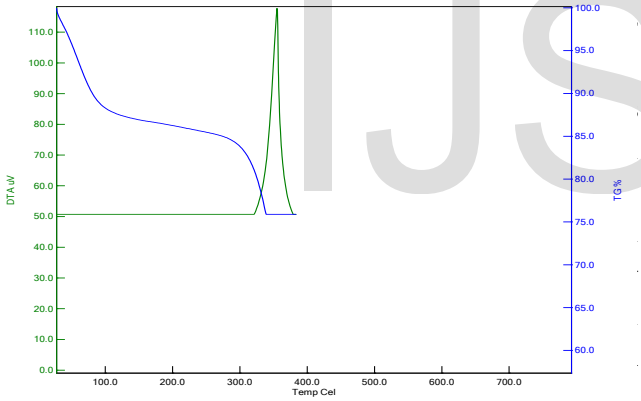
The TGA (fig.4) of the HAp/Polymer matrix nanocomposite powder was carried out between 30 to 800℃ in air at a heating rate of 25℃/min. The decomposition behavior of hydroxyapatite/ polymer matrix nanocomposite is shown in fig.4. The nanocomposite content is calculated from the residual weight in TGA curves at 550°C. However, since it is very difficult to control adsorbed water content in the composites. In the TGA curves several steps are observed (Rajendran et al. 2002; Singh et al. 2008; Wang et al. 2007). The first step, showing a small decrease in weight, is associated with adsorbed water – removing when heated above 90°C. The second step from 220 to 360°C may be due to the dehydraction reaction of C-OH groups in PVP chains. The DTA curve there is indication of endothermic sharp peaks at 360°C. Similarly the other endothermic peaks in the curve at 540°C. However in the starting at 60°C

a sharp exotherm indicates the crystallation of HAp.

Fig.4 Thermal analysis of nHAp/Polymer matrix.

4. Conclusion

Calcium phosphate (Hydroxyapatite) materials have been used extensively for bone



was carried out to investigate the thermal stability of the powder. The HAp with polymer powder produced can be highly useful as a bone replacement material.

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