

# Synthesis and Characterization of Nano Hydroxyapatite with Polymethyl methacrylate Nanocomposites for Bone Tissue Regeneration

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**Abstract:** Hydroxyapatite (HAp) is effectively used as a bioimplant material because it closely resembles bone apatite and exhibit good biocompatibility. The synthesis of HAp/PMMA nanocomposite has been prepared by wet chemical method. HAp/polymer nanocomposites are instances of these materials that can be used as bone cement, filling bone defects, coating of joint replacement prosthesis and dental implants. Several investigations have been studied on HAp/poly methylmethacrylate (PMMA) as potential bone cement. This material was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Transmission electron microscopy (TEM) and TG/DTA.

**Keywords:** FTIR, XRD, TEM, TG/DTA and PMMA

## 1. Introduction

Bone is an amazing nano composite of minerals and proteins. Finding a man-made nanocomposite that mimics natural bone has been desirable for many applications. Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is an interesting biomedical with potential orthopedic, dental and maxillofacial applications due to excellent biocompatibility, bioactivity, as well as osteoconductivity. HAp is used widely for hard tissues repair. As a result, this inorganic phosphate has been studied extensively for medical applications in the form of powder, composites or even coating [1-5]. Nano hydroxyapatite (nHAp) is chemically and structurally very similar to the inorganic component of bone, enamel, and dentin and has received considerable attention from biologists and biomedical scientist. It has been successfully used as bone fillers, coating of orthopedic implants, filler of inorganic / polymer composites among other applications. One of the most widely used methods is wet chemical precipitation, where chemical reactions take place between calcium and phosphorus ions under a controlled  $\text{p}^{\text{H}}$  and room temperature of the solution.

However, fast precipitation during titration of phosphate solution leads to the chemical homogeneity of chemical substances in the final product. Many types of polymeric materials have been used for bone tissue engineering [6, 7, 8]. They can be simply categorized as naturally derived materials (e.g. collagen and fibrin) and synthetic polymers (e.g. Poly (lactic acid) (PLA), Poly (glycolic acid) (PGA), and other co-polymer PLGA). However, synthetic polymeric materials have been widely used as bone cement, vehicle for cell transplantation and bone scaffolds for tissue engineering. Although these polymers have already been widely used in bone tissue engineering research. There are ongoing research efforts in improving the functionality of these polymers to further expand their applications. Other polymers have also been investigated for bone regeneration such as polyanhydrides [9, 10, 11], polycarbonates, polyphosphazene, polyfumarate, and poly (butylenes terephthalate) / poly (ethylene oxide). As a matter of fact,

natural bone matrix is an organic/ inorganic composites material of PMMA and hydroxyapatite. From this point of view, composite materials are better choices as bone tissue engineering scaffold [12]. It is well established that hydroxyapatite (HAp) mimics the natural bone mineral and has been found to possess good mechanical and osteoconductive properties [13]. For over 40 years, the best known polymeric material or biopolymer has been PMMA based bone cement. Typically, PMMA-based bone cement are employed in many orthopedic operations, e.g. in total joint replacement surgery, substitutes in vertebroplasty kyphoplasty, or as filling material in trauma surgery (Boyd et al., 200; Lewis, 2009). In joint replacement surgery, the main function of PMMA-based cement is to transfer body weight in order to increase the load-bearing and fixation capacity of the reconstruction area.

## 2. Materials and Methods

### 2.1 Materials

Nano hydroxyapatite has been synthesized through a microwave accelerated with a wet chemical method. The raw materials required to start the processing of the composite were: analytical grade calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and ammonium dihydrogen phosphate ( $(\text{NH}_4)_2\text{H}_2(\text{PO}_4)$ ) obtained from Merck (India) and Polymethyl methacrylate was purchased from Alfa Aesar. Doubly distilled water with ethanol was used as the solvent.

### 2.2 Methods

#### Synthesis of HAp and HAp - PMMA 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  $\text{p}^{\text{H}}$  of the solution was maintained from 9 to 11. The solution was constantly stirred 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 as - synthesized HAp powder (80) was mixed with polymer solution (20) where number denotes the wt% and the resultant HAp-PMMA composite powder was thoroughly mixed using a mortar and pestle for 30 min.

### 3. Results and Discussion

#### 3.1 FTIR

The FTIR spectra of pure nano HAp/PMMA composites are shown in figure 1. The FTIR spectrum investigation was carried out using Perkin Elmer spectrometer in the range of 400 - 4000  $\text{cm}^{-1}$ . The bands observed at 3432-3171  $\text{cm}^{-1}$ , (Kannan and Ferreira 2006), while the bands at 1638  $\text{cm}^{-1}$  overlap the -OH groups. The characteristic bands of PMMA, absorption of C=O, -CH<sub>2</sub>- appeared at 2432, 2356 and 1403  $\text{cm}^{-1}$  respectively. The bands located at 1036  $\text{cm}^{-1}$  is attributed to the PO<sub>4</sub><sup>3-</sup> groups. The frequency at 878  $\text{cm}^{-1}$  is the characteristic absorption of PMMA. The observed bands at 601  $\text{cm}^{-1}$  are due to phosphate bending vibration. The phosphate stretching mode is appeared at 566  $\text{cm}^{-1}$  corresponds to PO<sub>4</sub><sup>3-</sup> group. From these measurements, the precipitate particle is proved to be hydroxapatite with PMMA.

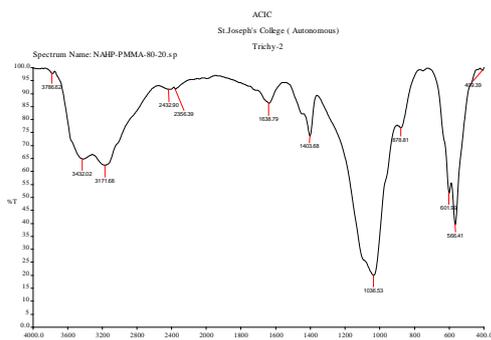


Figure 1: FTIR spectrum of HAp /PMMA Nanocomposite

#### 3.2 XRD

The reflection planes corresponding to the characteristic XRD spectral peaks of nHAp/PMMA composites are shown in figure 2. The observed diffraction peaks are identified by standard JCPDS (file no: 09-0432) file and are assigned as crystalline HAp. The main crystalline peaks observed for the composites at diffraction angles (002), (211), (202), (232) and (212) represent nHAp/PMMA composites. The XRD patterns show diffraction peaks with line broadening and high intensities which conforms the nano size to crystalline nature. The crystalline size of the pure nHAp-80/PMMA-20 composites is calculated by using scherrer formula.

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where D is the crystalline size calculated for the (h k l) reflection,  $\lambda$  the wavelength of CuK $\alpha$  radiation (1.5406Å),  $\beta$  the full width of the peak at half of the maximum intensity

(FWHM) and  $\theta$  the diffraction angle of the corresponding reflection.

The fraction of crystalline phase ( $X_C$ ) of the HAp powders was evaluated by the following equation (Londi et al 2000)

$$X_C = \frac{1 - V_{211/202}}{I_{202}}$$

Where  $I_{202}$  is the intensity of (202) diffraction peak and  $V_{211/202}$  the intensity of the hollow between (211) and (202) diffraction peaks of HAp.

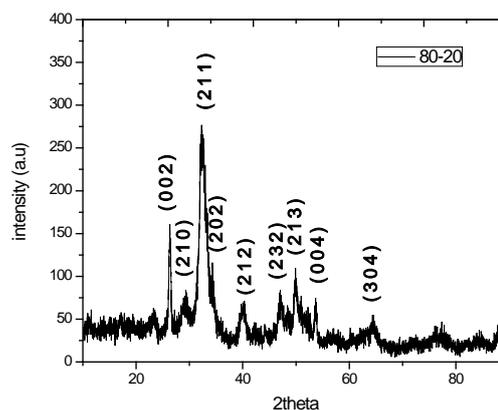
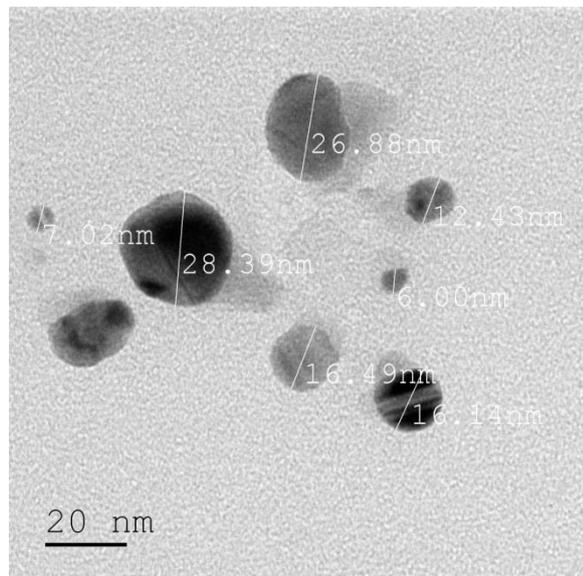


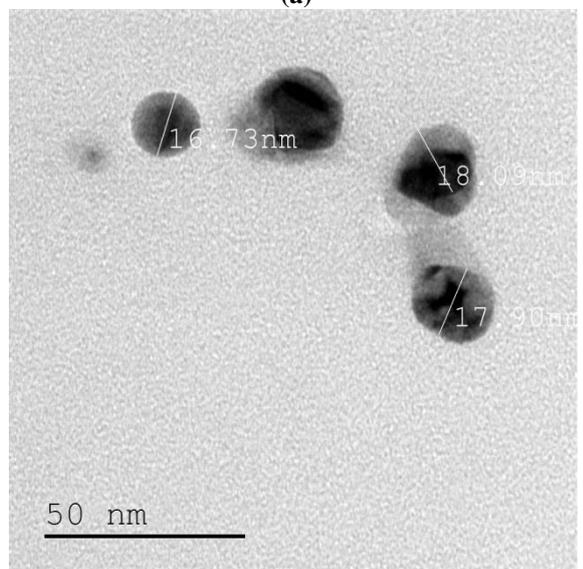
Figure 2: XRD of HAp/PMMA Nanocomposite

#### 3.3 TEM

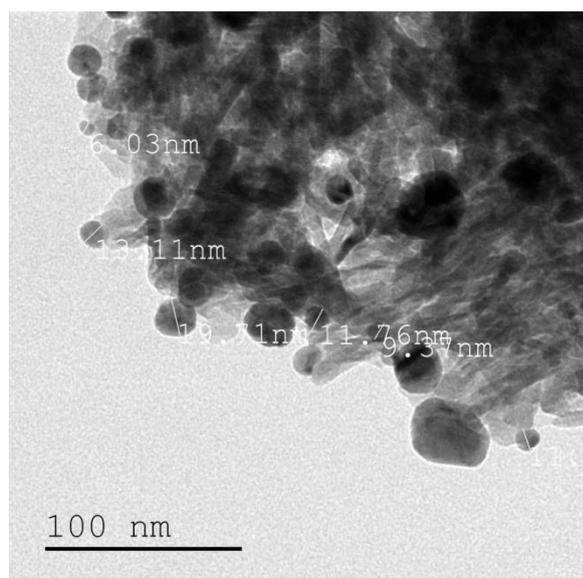
The morphology and the particle size of synthesized nHAp/PMMA in different composition of HAp-80, PMMA-20 is shown in figure 3(a), (b) and (c). The morphology depicts the spherical image of nHAp/PMMA powder in the nanometer range, being length of 20 to 100 nm. The TEM image fig 3(c) shows the presence of agglomerations among particles, which are due to the high specific surface energy of nHAp particles with homogeneous dispersion. They are well identified in case of the HAp/PMMA composites fig (3). The particle size of HAp is controlled by the polymer (PMMA) in the composites as depicted in the TEM micrograph which are due to the very fine size of precipitated particles present in the aggregates. They could not be individually resolved, however, these crystalline nature and phase identification could be ascertained through selected area electron diffraction (SAED) pattern which confirm the formation of nHAp. In some regions nearer to 20-50nm, there is almost no agglomeration, which may be due to reduction of surface energy of nHAp using polymer (PMMA) through its pendent phosphate group. This is well responsible for the improvement of the mechanical properties of the HAp/PMMA nanocomposite over the pure PMMA polymer.



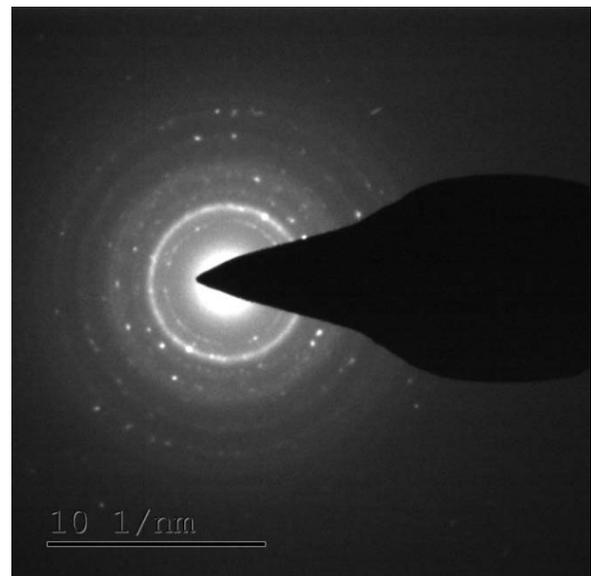
(a)



(b)



(c)

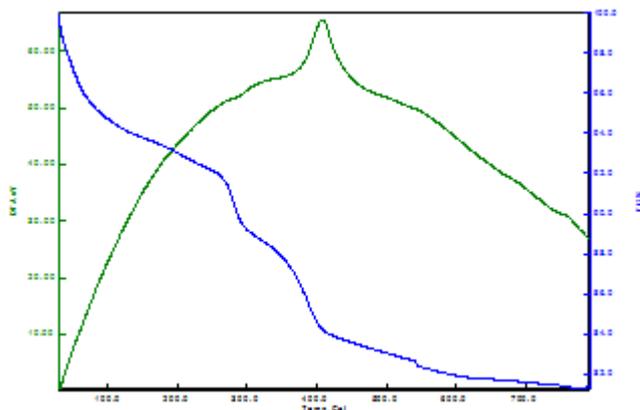


(d)

**Figure 3:** (a), (b), (c) TEM images of HAp/PMMA nanocomposite and (d) is selected area electron diffraction (SAED)

### 3.4 TG/DTA

The Thermal gravimetric (TG) analysis is performed in an atmosphere (i.e.) air (or) oxygen with a linear ramp temperature. The maximum temperature showed be so selected that the weight of the specimen is stable at the end of the experiment. Thermal stability of as synthesized nanoHAp/PMMA was analyzed using Perkin Elmer experiment for TG-DTA. The TG of the HAp/PMMA nano composites powder was carried out between 30 °C to 800 °C in air at a heating rate 25 °C /min. The decomposition behaviour of HAp/PMMA nano composite is as shown in fig.4. In the TG 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 80 °C. The second step, from 190 °C to 380 °C may be due to the C-OH groups. This temperature shifts to a higher temperature, when the nano HAp content increases. In DTA curve initially, there are series of small curves occurs which is followed by a broad curve between approximately (200 °C to 300 °C). This is occurring because evaporation of water in calcium hydroxide happens. Similarly the other endothermic peaks in the curve (305°C to 420°C) related to the removal (or) addition of their groups during the synthesis of HAp/PMMA powder. However in the starting at 150°C a sharp exotherm indicates the crystallization of HAp.



**Figure 4:** DTA-TG analysis of synthesized HAp/PMMA Nano composite

#### 4. Conclusion

The biodegradable polymers properties do give definite impact on the bone healing, formation, regeneration (or) substitution for human body. Nano hydroxyapatite / PMMA have been successfully synthesized using the wet chemical method. The HAp composites when examined by FTIR spectroscopy clearly show the presence of HAp and polymer components in the composite. The XRD studies also confirm the nano sized HAp powder in native state as well as in composites. The size and morphology of the samples were characterized using by transmission electron microscopy. The spherical shaped particles were confirmed through the TEM analysis. Thermal properties of the material assigned by DTA/ TG analysis, meet the thermal requirement of these types of materials. In addition, at the implantation period, assessed, the extent of newly formed bone on the polymeric regeneration on HAp implants. These findings indicate that the tested polymers are suitable scaffolds for a bone tissue engineering approach in the treatment of bone defects.

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