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SYNTHESIS AND CHARACTERIZATION OF NANO HYDROXYAPATITE WITH POM AND PVP NANOCOMPOSITE USING FOR BONE TISSUE ENGINEERING

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ABSTRACT

In recent years, several kinds of polymer – hydroxyapatite nano composites have been developed as bone substitute materials. The purpose of making such composites is to reinforce the polymer and improve the bone bonding properties of the materials, since it has been found that adding hydroxyapatite into a polymer matrix (POM with PVP). Therefore, there is a growing need for the development of nanocomposites with biocompatibility and bioactivity. Comparisons with pure nHAp/polymer matrix prepared by wet chemical precipitation method. The main goal is to highlight the efforts of the introduction of polymers on the physicochemical properties, morphology and biocompatibility for applications in bone surgery.

KEYWORDS: FTIR, XRD, TEM, TG/DTA.

INTRODUCTION

Hydroxyapatite (HAp) is main inorganic part in the bone composition and has been used as popular implant materials in the field of bone surgery. [1] Recently, a great deal of interest has been directed towards creating bioactive ceramic/polymer composites to be used as bone grafting materials. It is well known that synthetic bone is an inorganic/organic composite material. Therefore, there is a growing interest in composite materials. As reported by previous authors, mixture of HAp with polymer has been found to be an effective formulation technology to gain the intelligent artificial bone materials [2-4]. Synthetic polymers were studied as potential matrices of composite materials with hydroxyapatite (HAp) filler for possible application as bone analogues: polymethyl methacrylate (PMMA), polyethylene (PE),

polypropylene (PP), polyurethane (PU) [5-6]. At present, HAp is the major calcium phosphates used in clinic. Currently, HAp/POM with PVP is used primarily as bioactive coatings on bioinert materials like bone tissue repair, bone tissue regeneration, bone implants as well as for drug delivery purpose. Recently, several attempts have been made to develop nanocomposites, where in nHAp particles are embedded in polymer matrix.

The combination of calcium phosphates (HAp) and synthetic polymers (Polyoxymethylene (POM) and Poly Vinyl Pyrrolidone (PVP)) to develop suitable bone substitutes has been intensively investigated and many researchers have been done to give the biocompatible, bioactive, biodegradable and osteoconductive properties of the synthetic bone (Itoh et al., 2002). 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 poly anhydrides, poly carbonates, poly phosphazene and poly (butylenes terephthalate) [7, 8, 9]. Polymeric biomaterials have several important uses in addition to tissue reconstruction. Examples include poly (methyl methacrylate) bone cement, poly (glycolic acid) degradable sutures, poly (glycolic-co-lactic acid) bone screws and poly vinyl siloxane dental impression materials. It is well known that the two fundamental factors to be considered in producing polymer nanocomposites with bone – like properties are (i) good interfacial adhesion between organic polymers and inorganic hydroxyapatite (HAp) and (ii) uniform dispersion of HAp at the nano level in the polymer nanocomposite (Lee et al. 2007).

MATERIALS AND METHODS

Materials

The raw materials required to start the processing of the composite were: analytical grade Calcium hydroxide ($\text{Ca}(\text{OH})_2$) was purchased from Sigma Aldrich and ammonium dihydrogen phosphate ($(\text{NH}_4)_2\text{H}_2\text{PO}_4$) procured from Mercy (Mumbai, India). Polyoxymethylene were purchased from Alfa Aesar and Poly vinyl pyrrolidone (Mw 40000) was purchased from Sigma Aldrich. Doubly distilled water with ethanol and hot water was used as the solvent.

METHODS

Synthesis of HAp/POM 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 p^{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 synthesized HAp powder (80) was mixed with polymer matrix solution (20) where number denotes the wt% and the resultant HAp - POM and PVP composite powder was thoroughly mixed using a mortar and pestle for 30 min.

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of pure nHAp with POM and PVP nano composites are shown in fig.1. The FTIR spectrum investigation was carried out using Perkin Elmer spectrometer in the range of $400 - 4000\text{ cm}^{-1}$. The observed peak at 3430.80 cm^{-1} corresponding to the stretching mode of $-\text{OH}$ group, which characterized the presence of calcium phosphate such as HAp. The characteristic bands of POM absorption are observed at 2955.47 cm^{-1} , 2483.66 cm^{-1} , 1429.63 cm^{-1} and 1292.31 cm^{-1} . The presented peaks (Urch et al 2009) of PVP, absorption of $\text{C}=\text{O}$, $\text{C}=\text{N}$ appeared at 1233.31 cm^{-1} and 1659.49 cm^{-1} respectively. The bands located at 1031.85 cm^{-1} is attributed to the PO_4^{3-} groups. The strong peaks at 1429.63 cm^{-1} corresponds to the stretching vibration of CO_2^{3-} . The phosphate stretching mode appeared at 563.32 cm^{-1} corresponds to PO_4^{3-} groups.

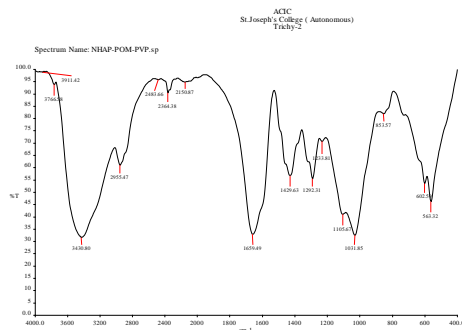


Fig.1. FTIR spectrum of nHAp with polymer matrix.

XRD Analysis

The phase analysis is performed from the recorded X-ray diffraction pattern of HAp with polymer matrix as shown in fig. (2). Crystallite size and crystallinity of HAp with polymer matrix were investigated with powder XRD spectrum and broaden diffraction peaks are $2\theta = (25.8), (29.7), (31.8)$ and (34.5) these peaks are assigned to the miller's indices reflection planes are (002),(210),(211) and (310) with the XRD pattern of complete polymer matrix showed three characteristic reflection planes. These plane (202), (213) and (004) indicate that the ranging crystallite size is very small from (20-50) nm. This XRD spectrum indicates most of the high intensity peaks positioned between $2\theta = 25^\circ - 34^\circ$ were observed the peak broadened. This indicates that synthesized HAp with polymer matrix crystallites are present in nano scale level. The results of XRD analysis obtained in the present investigation are good agreement with the reported results (Bouyer et al., 2000)

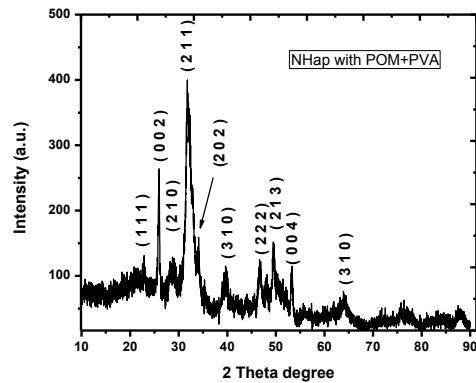
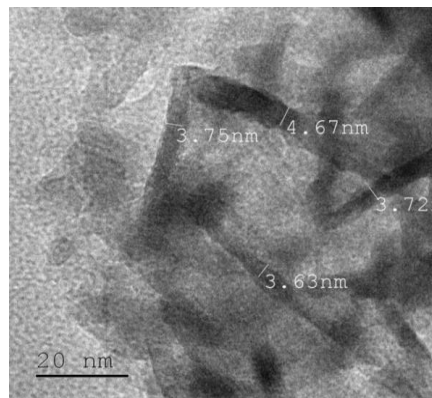


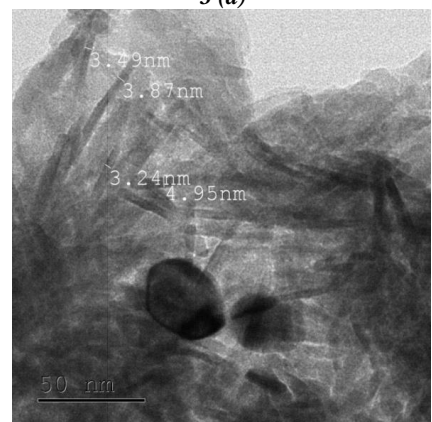
Fig.2. XRD of nHAp/ polymer matrix

TEM Analysis

The structure and morphology of the samples were further confirmed by the TEM image of the prepared nano hydroxyapatite with polymer matrix as shown in fig. (3). The transmission electron microscopic analysis confirms the presence of the rod-like morphology of the samples with the particle size of around 20 to 50 nm. The particle size is also found to be in agreement with the report results of (Ferraz et al., 2004). According to TEM analysis, the particle is homogeneously dispersed in polymer matrix. In addition the selected area electron diffraction (SEAD) of the precipitates shows with diffraction ring of patterns, which implies that the precipitates are crystalline in nature. This is agreed with XRD results.



3 (a)



(b)

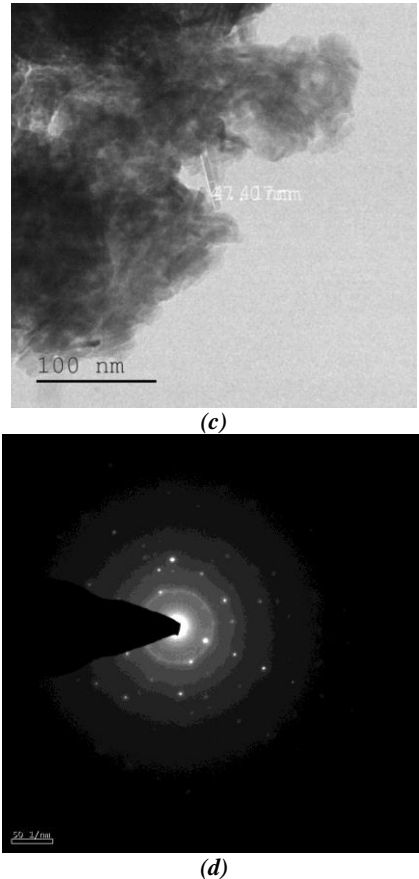


Fig.3 (a), (b), (c) TEM images and (d) Selected Area Electron Diffraction (SAED) image of nHAp/Polymer matrix.

TGA/DTA

Thermal stability of synthesized nano HAp/POM and PVP was analyzed using the Perkin Elmer experiment for TGA/DTA. TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate) or as a function of time (with constant temperature and /or constant mass loss). The TG of the HAp/POM with PVP nano composites powder was carried out between 30°C to 800°C in air at a heating rate 25°C /min. The TG analysis shows that there is weight loss of around 10% up to temperature 120°C then 8% in the range 380°C and 7% in the range 420°C. Fig.4 shows a continuous mass loss of the HAp by an increase in temperature 400°C and 500°C in the presence of polymer concentration.

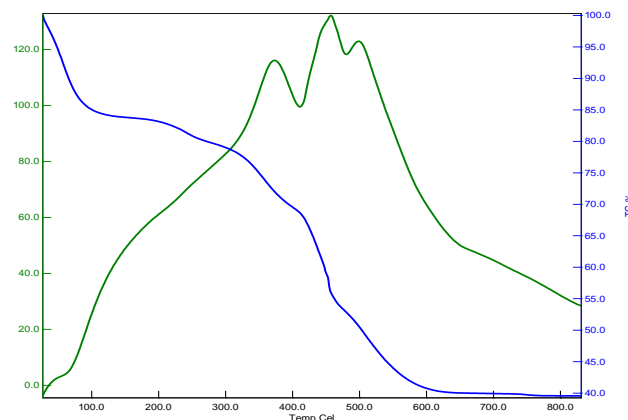


Fig.4. TGA/DTA analysis of synthesized nHAp with polymer matrix.

CONCLUSION

The review articles deals with some of the calcium phosphate (HAp) with polymer matrix materials which are currently used in bone tissue engineering. nHAp/ POM and PVP have been successfully synthesized using the wet chemical method. The nanocomposites when examined by FTIR spectroscopy clearly show the presence of HAp and polymer matrix components in the composite. The formation of nHAp/polymer matrix nano particle was confirmed by the X-ray diffraction (XRD). 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. Although, nHAp with polymer matrix materials excellent bioactive and biocompatibility properties of the results in bone formation in a host and strong biological fixation to bone tissue engineering.

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REFERENCES

- [1] J. Huang, Bes SM, Bonfield W, et al. *J mater sci mater med*2004; 15(4): 441-445
- [2] Y. Shikinami, okuno M. *Biomaterials* 2001; 22(23): 3197 – 3211.
- [3] M. Wang, Bonfield W. *Biomaterials* 2001; 22(11): 1311-1320
- [4] Petricca SE, Marra KG, Kumta PN. *Acta-Biomater* 2006; 2(3): 277-286
- [5] M. supova, Problem of hydroxyapatite dispersion in polymer matrices: a review. *J Mater sci mater med.* 2009; 20: 1201-1213; and references herein. doi: 10.1007/s/0856-0856-3696-2.
- [6] S. Bertoldi fare S, ciapetti G, Tanzi; MC polyurethane foams and Ca-P composites for bone tissue engineering. *J app Bioo mater Biomech.*2007; 5(3): 195.
- [7] Hanes, J., M. Chiba, and R. Langer. Degradation of porous poly (anhydride-co-imide) microspheres and implications for controlled macromolecule delivery. *Biomaterials* 19:163–172, 1998.
- [8] Ibim, S. M., K. E. Uhrich, R. Bronson, S. F. El-Amin, R. S.Langer, and C. T. Laurencin. Poly (anhydride-co-imides): in vivo biocompatibility in a rat model. *Biomaterials* 19:941–951, 1998.
- [9] Uhrich, K. E., A. Gupta, T. T. Thomas, C. T. Laurencin, and R. Langer. Synthesis and characterization of degradable poly (anhydride-co-imides). *Macromolecules* 28:2184–2193, 1995.