International Journal of Pharmacy and Biological Sciences
ISSN: 2321-3272 (Print), ISSN: 2230-7605 (Online)
IJPBS | Volume 8 | Special Issue 4-Chem Fest | 2018 | 123-128
2nd National Conference on Emerging Trends and Future Challenges
In Chemical Sciences-Chem Fest-18
Held at Shanmuga Industries Arts and Science College, Tiruvannamalai, 05th Oct 2018
| Seminar Proceedings | Research Article | Biological Sciences |Open Access |MCI Approved|
|UGC Approved Journal|

SURFACTANT AND POLYMER ASSISTED SYNTHESIS OF HYDROXYAPATITE USING SONOCHEMICAL METHOD

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ABSTRACT

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is one of the well-known bioceramic material which has its therapeutic applications as a bone substitute material because it is structurally similar to human bone. It also has excellent biocompatibility, bioactivity and surface-active properties with living tissues, osteoconductivity and non-toxicity. Particularly, this material is employed in orthopaedic and dental applications. In this research, hydroxyapatite powder was synthesized by doping with polyplasdone polymer and polyoxyethylene lauryl ether (Brij-35) as a surfactant through sonochemical method. By passing an ultrasound HAP powder is obtained with high degree of crystallinity, purity with minimal agglomeration. The Ca/P ratio is very nearest to the stoichiometric value. This work reports synthesizing nano-HAP powder using templates through sonochemical method by tuning the experimental parameters such as irradiation time, temperature and concentration of the mixture. Owing to its bioactivity, it has been proven that polymer assisted surfactant assisted calcium phosphate synthesis structure gave pure nanobioceramic powders with high degree of crystallinity after calcination. The as synthesised powder is to be tested further for this biocompatibility.

KEY WORDS

Hydroxyapatite, Ultrasound, POELE, Polyplasdone

1.INTRODUCTION

Hydroxyapatite is the main inorganic constituents of bone and teeth [1]. Hydroxyapatite is commonly referred to as HAP. Synthetic hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$) is commonly used in orthopaedic applications due to its very high biocompatibility, bioactivity, and osteoconductive properties and it favours the formation of new bone growth in osteoblastic cells [2-3]. Specifically, in orthopaedic applications, hydroxyapatite is used in a fabricated and sterilized form to improve the bioactive properties the importance of HAP has led to extensive research in numerous areas ranging from the physicochemical mechanisms of the formation to its applicability as a biomedical or industrial material [4-7]. In particular, the biocompatibility and osteoconductive properties of HAP have made it useful as implant material. New developments on the production of nano-sized HAP particles have led to many new applications. For example, nano-sized HAP particles can retard the multiplication of cancer cells and be used as an efficient drug delivery agent [8-9]. In orthopaedic applications, hydroxyapatite is used in a fabricated and sterilized form to improve the bioactive properties. The structural and morphological properties is depending on temperature, time and ratio of calcium phosphate solutions. There are a number of significant advantages by using synthetic HAP in hard tissue industrial applications due to its good biocompatibility and bioactive properties with respect to bone cells and

other body tissues, a slow biodegradability in situ and it also offers good osteoconductivity and osteoinductivity capabilities [10 - 12]. Now it has been reported that the surfactant and polymer assisted synthesis of hydroxyapatite using sonochemical method is the most promising method for the preparation of hydroxyapatite by novel morphologies and properties. There are 3 stages in ultrasound when proceeds to the reaction mixture including formation, growth and ends with implosive collapse of bubbles. It depends on the reaction stimulated by powerful ultrasound radiation leads to the creation of acoustic cavitation, continuous formation, growth and implosive collapse of the bubbles in a liquid [13-15]. It also stimulates the reaction between calcium and phosphate precursors accelerate the reaction rate in a significant manner [16-17]. In this research, by adding surfactant and polymer, nanosized products are induced, surface morphology and size are perfectly controlled with high porosity. The structural feature of the HAP powder was evaluated by using FTIR, XRD and SEM.

2. MATERIALS AND METHODS

2.1 CHEMICALS AND REAGENTS

The novel synthesis of HAP nanoparticle was achieved by using dual templates and ultrasound method. Calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$ as well as diammonium hydrogen phosphate $(NH_4)_2\ HPO_4$, polyplasdone and polyoxyethylene lauryl ether and aqueous ammonia. Were used Deionised water was used throughout the synthesis process. All the chemicals received were of analytical grade and obtained from Merck.

2.2 SYNTHESIS OF HYDROXYAPATITE BY TEMPLATES ASSISTING SONOCHEMICAL METHOD

Initially, the synthesis of nanohydroxyapatite was begun by taking 1M of Calcium nitrate tetrahydrate with 0.5 g of polyplasdone, varying amount of POELE (0.001M-0.003M) was dissolved in 20ml of deionized water is taken in a separate beaker, stirred well for 5 minutes until the solid particles are invisible. Followed by 0.6M of diammonium hydrogen phosphate is taken in a separate beaker and dissolved in 20 ml of deionized water. The mixture of phosphate salt solution was added dropwise to the solution containing Calcium nitrate tetra hydrate solution with vigorous stirring. The stoichiometric ratio of Calcium and phosphate was maintained at 1.67. The solution mixture was maintained at constant pH 10 by adding aqueous ammonia solution and the resulting suspension was stirred using magnetic stirrer for an hour. After continuous stirring a homogeneous and transparent solution was obtained. The white suspension obtained was irradiated with an ultrasound for about 40 minutes at 70℃, a transparent dispersion was obtained. The resulting suspension was kept for aging for 48 hours. Then precipitate remains separated from the supernatant liquid and washed with 1:1 ratio of deionized water and ethanol. The precipitate was dried in hot air oven at 80℃ for 10 hours to attain a fine powder. Finally, the resulting powder was then calcined for about 4 hours in silica crucible and sintered in muffle furnace to obtain pure HAP powders.

2.3. CHARACTERISATION

Fourier transform infrared spectroscopy (Perkin- Elmer) is a spectroscopic technique which is used to identify the functional groups especially phosphate and hydroxyl groups in calcium phosphate. The spectrum was recorded in the wave number region of 4000-400 cm^{-1}. The crystallinity and phase analysis of the sample were carried out using XRD. The size of the crystal is calculated using Scherrer formula. The surface morphology of the sample was investigated using scanning electron microscopic technique.

3.RESULT AND DISCUSSION

3.1 FTIR ANALYSIS OF HYDROXYAPATITE POWDER

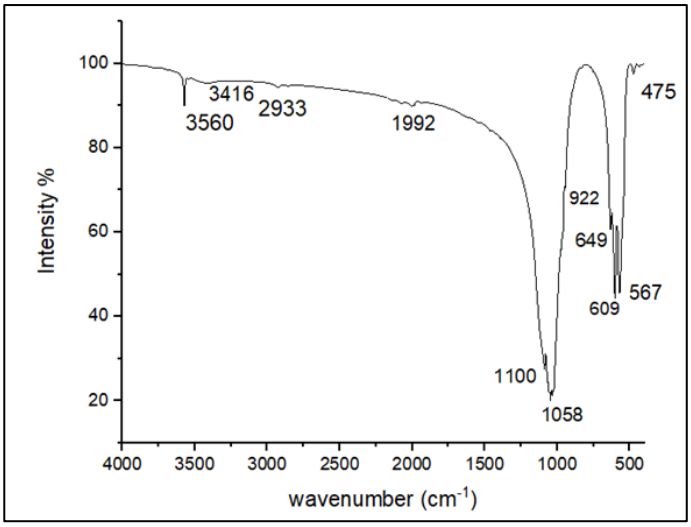

Fig3.1 (a) FTIR analysis of polymer assisted hydroxyapatite powder without ultrasound

The HAP structure contains OH and PO_4 group. In **Fig.3.1 (a)** The sharp band situated at 3560 cm^{-1}, 649 cm^{-1} indicates O-H functional group, at the wavenumber 3416 cm^{-1} corresponds to hydroxyl groups of bending mode. The band situated at 1100 cm^{-1} and 1058 cm^{-1}indicates ν_3 modes of phosphate groups, 609 cm^{-1} and 567 cm^{-1} are assigned to be (ν_4) mode of phosphate groups, 475 cm^{-1}can be assigned as (ν_2) modes of phosphate group of HAP. The band obtained at the wavenumber 922 cm^{-1} indicates (ν_1) mode of phosphate group. The peak located at 2933 cm^{-1} and 1992 cm^{-1} are due to presence of CH_2 groups respectively.

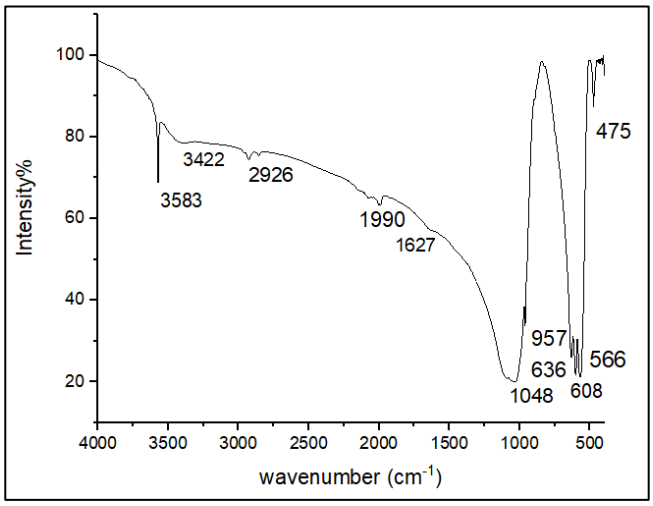

Figure 3.1 (b)FTIR spectrum of HAP assisted with POELE without ultrasound

The HAP structure contains OH and PO_4 group. In **Fig.3.1 (a)** The sharp band situated at 3583 cm^{-1}, and 636 cm^{-1} the indicates O-H functional group, and the broad peak at 3422 cm^{-1} corresponds to hydroxyl group. The band situated at 1048 cm^{-1}indicates ν_3 modes of phosphate groups, 608 cm^{-1} and 566 cm^{-1} are assigned for ν_4 mode of phosphate groups, the peak at 475 cm^{-1}can be assigned to ν_2 modes of phosphate group of HAP. The band obtained at the wavenumber 957cm^{-1} indicates ν_1 mode of phosphate group. The peak located at 2926 cm^{-1} and 1990 cm^{-1} are due to presence of CH_2 groups respectively.

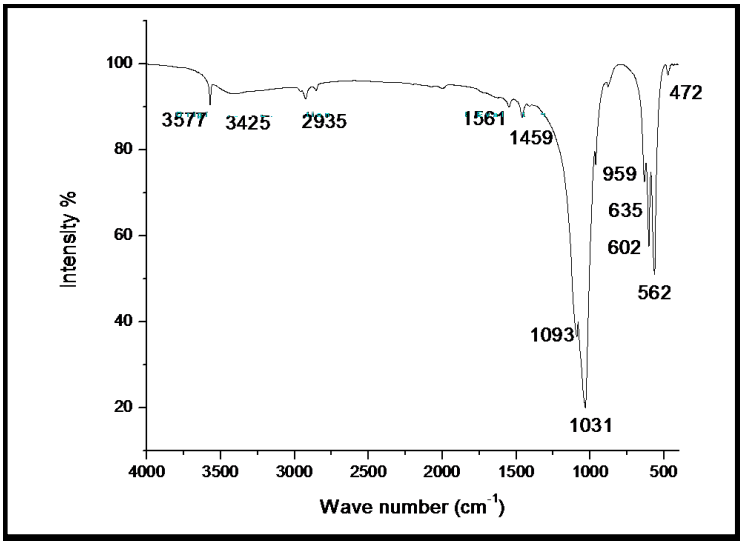

Fig 3.1 (c) FTIR spectrum of HAP assisted with Polyplasdone, POELE with ultrasound method

FTIR spectra of polyplasdone, POELE and ultrasound assisted hydroxyapatite powders are shown in **Fig.3.1 (c)**. The peaks at 3425cm^{-1}, 1622cm^{-1} were due to the bending mode of the absorbed water, while the sharp peak at 3577 cm^{-1} is assigned to the stretching vibration of the lattice OH^- ions, and a medium sharp peak at, 635 cm^{-1} is detected as -OH group of HAP. Obviously, the vibration peaks of $-CH_2$ stretching mode observed at 2935 cm^{-1}. The characteristic bands at 472 cm^{-1}, 562 cm^{-1}, 602 cm^{-1}, 959 cm^{-1}, 1031 cm^{-1}, 1093cm^{-1} corresponds to phosphate groups respectively.

3.2. XRD CHARACTERISATION OF HYDROXYAPATITE POWDER

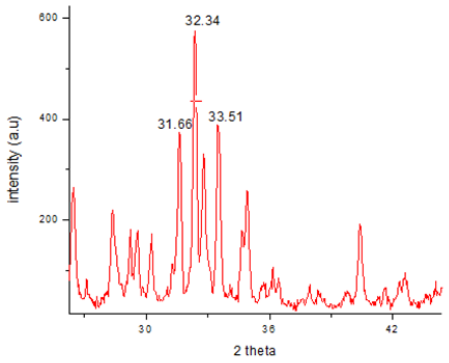

Fig: 3.2.(a)

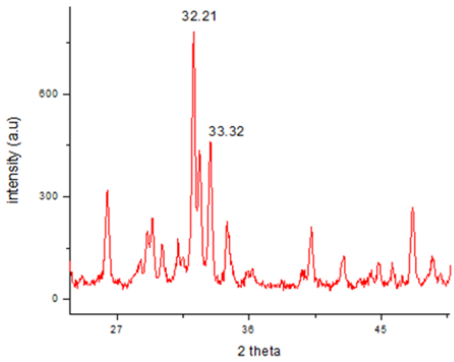

Fig: 3.2.(b)

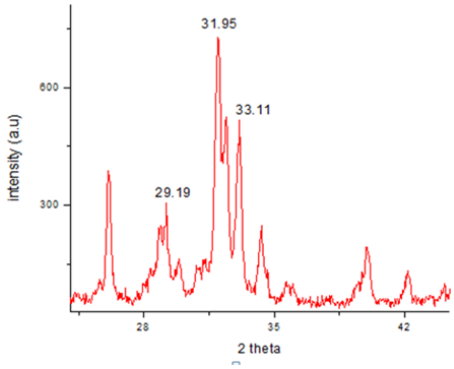

Fig: 3.2.(c)

Fig.3.2 XRD pattern for HAP assisted with (a) Polyplasdone(b)POELE (c) Polymer, POELE and ultrasound technique.

The powder diffraction and phase analysis were carried out by powder X-ray diffractometer. XRD pattern of the polymer assisted HAp sample are shown in **Fig 2a)**. The sharp peak appears at 32.34, 31.66, 33.51 does not alter much indicating that the peak remains at apatite phase. **Fig: 2 (b)** indicates the XRD pattern for surfactant assisted HAP formed. From the figure, we observed that, the high intense peak at 32.21,33.32 value are assigned as calcium phosphate powder. In **Fi: 2(c)**, the 2θ value appears at 31.95, 33.11 is obtained by assisting polymer, POELE and ultrasound. Finally, by assistance polymer, surfactant and ultrasound, it was observed that the purity gets increased. The synthesised hydroxyapatite sample value is similar to the JCPDS Card (09-0432) value, which indicates that the crystal structure of HAP sample is similar to pure hydroxyapatite. The polymer, surfactant and ultrasound assisted the formation of hydroxyapatite grain size, which gets decreased when compared to **(Fig. a and b).** The grain size was calculated by Scherrer equations.

3.3 SCANNING ELECTRON MICROSCOPIC STUDIES

The surafce morphology and crystallite morphology of the synthesised material were investigated by scanning electron microscopic technique (SEM).

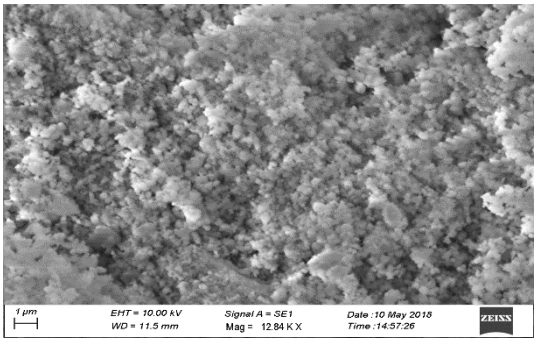

Fig: 3.3(a) Polymer without Ultrasound

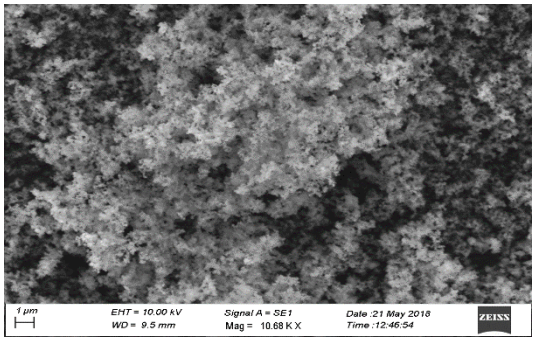

Fig: 3.3 (b) POELE without surfactant

SEM image of polyplasdone assisted hydroxyapatite nanoparticles prepared without ultrasound method are shown in **Fig 3.3 (a) and (b).** SEM micrograph shows spherical like structure with 1µm in size. The **Fig 3.3 (a) and (b)** are highly aggregated and nonuniform size and morphology, and also the particles are not homogenously dispersed on the surface of HAP nanocomposite without ultrasound.

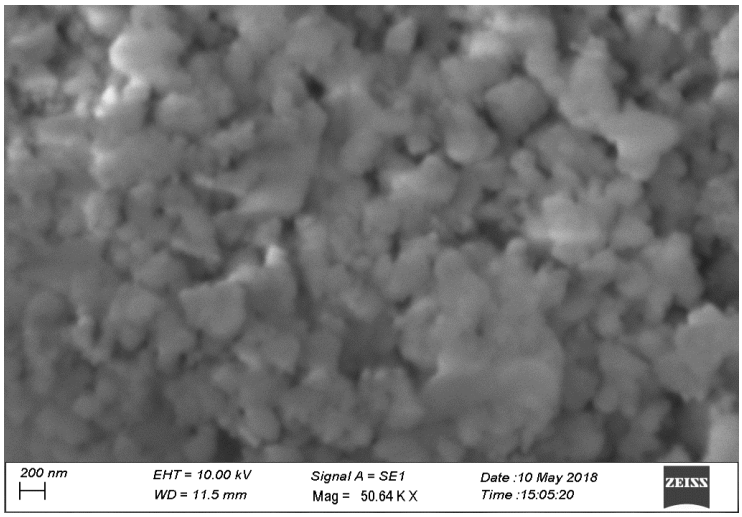

Fig 3.3 (c): SEM micrographs of HAP composite armoured with Polyplasdone, POELE and ultrasound technique.

The SEM micrograph of HAP nanomaterial synthesized using Polyplasdone, POELE with ultrasound technique is shown in **Figure 3.3 (c).** The SEM images of nanoparticles are formed by assisting Polyplasdone, POELE with ultrasound method when compared to **Fig 3.3 (a) & (b).** It is evident that HAP particles are spherical

like appearance and almost uniform size. The size of the particles has increased indicating more material formation. The average particle size of non-ultrasound sample is about 1µm, while average particle size with ultrasound samples are 200nm respectively.

CONCLUSION

In the present study, the synthesis of hydroxyapatite composite powders with polyplasdone as a template and POELE as surfactant were successfully synthesized by using son chemical method. It has also been established that the non- ionic surfactant POELE can be used to control morphology and crystallinity of HAp nanopowders. The incorporation of sonication process was found to enhance the chemical reaction, the product formation and improve the quality of polymer composite with surfactant synthesis of hydroxyapatite powders in terms of particle size reduction with different surfactant concentrations. The synthesized powders were found to be pure and free from impurities which are confirmed by FTIR, XRD and SEM studies.

ACKNOWLEDGEMENT

One of the authors (Dr. V. Collins Arun Prakash) thank the Abraham Panampara Research centre (APRC), Sacred Heart College (Autonomous) Tirupattur, for the financial assistance through received under “Don Bosco grant” scheme.

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