International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Synthesis and Characterization of Hydroxyapatite with Gum Arabic (Biopolymer) Nano Composites for Bone Repair

K. Senthilarasan[1] , P. Sakthivel[2]

[1, 2]Department of Physics, Urumu Dhanalakshmi College, Tiruchirappalli, Tamilnadu, India-.620019

Abstract: ***In this present study, nano particles with two phases Hydroxyapatite and Gum Arabic (nHAp/GA)were prepared using modified wet chemical method.Hydroxyapatite (HAp) is a biocompatible ceramic that is widely used in a number of biomedical applications and devices. Due to its close similarity with natural bone matrix in nanometer scale, research is carried out to study its reaction with biopolymer at this scale. HAp and mineral phase found in the natural bone matrix, Gum Arabic(GA), a kind of plant-polysaccharides , were used to improve the property of artificial bone matrix and widely used for pharmaceuticals purposes. These composite were Characterized by FT-IR, X-ray diffraction,Transmission electron microscope techniques and thermal analysis. The crystallite size, lattice parameters, specific surface area , volume density, microstrain, 'u' parameter and dislocation density were also measured by using XRD data.***

Keywords: Hydroxyapatite, Gum Arabic, XRD, FT-IR,TEM, TG/DTA

1. Introduction

Bone is the most implanted tissue after blood, and its major solid components are collagen, hydroxyapatite, glycoprotein and proteoglycan[1]. Hydroxyapatite is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3OH$, but is usually written as $Ca_{10}(PO_4)_6OH_2$ to denote the crystal unit cell.HAp is the hydroxyl endmember of the complex apatite group. The OH^- ion can be replaced by fluoride, chloride or carbonate, producing fluorapatite, chlorapatite. It crystallizes in the hexagonal crystal system. Pure hydroxyapatite powder is white. Naturally occurring apatites can however, also have brown, yellow or green colorations, comparable to the discolorations of dental fluorosis.[2] HAp Based bioceramics are successfully used as implants as they are chemically similar to the inorganic constituent of biological hard tissue. HAp is also a potential implant material due to its excellent osteoconductive properties. HAp is widely used for bone implant and bone cement applications due to its compositional and biological similarties to native tissues. The application of HAp as useful biocompatible materials largely depends on the purity and morphology of the powder. HAp can be prepared by different routes like chemical precipitation, sol-gel route, combustion synthesis, plasma, etc. The purity in the final HAp powder and stoichiometry ratio of Ca/P = 1.67 can be well controlled by the chemical precipitation route.[3]HAp has been studied extensively and prepared for clinical applications involving artificial bones and teeth, because of their high biocompatibility, bioactivity, ability for biodegradation and mechanical properties.[4]

Acaica gum, also called Gum Arabic (GA), is a complex arabinogalactan -type polysaccride exuded by Acacia trees.[5] Gum Arabic (GA) is a branched chain,consists of complex polysaccharide, either neutral or slightly acidic. The polysaccharide acid consist of the salts like calcium,magnesium and potassium The backbone is composed of 1,3-linkedβ-D-galactropyranosyl units. The side chains are composed of two to five 1,3 linked β- D-galactopyranosyl units, joined to the main chain by 1,6 – linkages.[6] GA a natural polymer which is known for its usage in controlled drug delivery systems.[7] GA is widely used for its nutritional and surface properties by the food industry in microencapsulation or complex coacervation processes in pharmaceutics, cosmetic or ink, but also in lithographic explosives and textiles.[5] In folk medicine, GA has been reported to be used internally for the treatment of inflammation of the intestinal mucosa, and externally to cover inflamed surface. Despite the fact that GA is widely used as a vehicle for drug in experimental physiological and pharmacological experiments, and is assumed to be an inert substance, some recent reports have claimed that GA possesses anti-oxidant, nephroprotectant and others effects [6]

2. Experimental Design

2.1 Materials

In present study a simple modified wet chemical method was proposed to prepare nano sized HAp powder using Calcium hydroxide $Ca(OH)_2$ and Ammonium dihydrogen phosphate $(NH_4)_2PO_4$,that were obtained from Merk (India). Gum Arabic Powder was purchased from Loba(India). Ethanol and double distilled water were used as the solvent.

2.2 Synthesis of nanoHAp

Nano HAp was synthesized by following, a modified wet chemical method. At room temperature, 5.56 g of calcium hydroxide was first dissolved in a 100 ml volume of an ethanol-water mixture (50:50%,v/v) and stirred for 3h. A solution of 6.7 g $(NH_4)H_2PO_4$ was dissolved in 100 ml volume of water and then added to the $Ca(OH)_2$ solution over a period of 24 hours. The amount of reagents in the solution was calculated to obtain a Ca/P molar ratio value equals 1.67, corresponding to a Stoichiometric HAp. The pH of the slurry was measured digitally during the precipitation reaction, reaching a final value of pH 11.

2.3 Synthesis of nHAp / Gum Arabic composite

Gum Arabic was dissolved in double distilled water and thenaddednHAp powder. The sample was continuouslyrotated usingby Magnetic stirrer. Finally, the sample was dried using by microwave oven.

3. Characterization

a) FTIR
The Fourier transform infrared (FT-IR) Spectra were recorded on a Perkin Elmer Spectrometer, in the range of 400 cm^{-1} to 4000 cm^{-1}.

b) XRD
X-Ray diffraction studies of the powdered sample were carried out for phase identification using X-ray diffractometerRigaku with monochromatic CuKα radiation (λ=1.5405Å) . The powder sample were scanned in the Bragg angle,2θ range from 10-90°.

c) TEM
Transmission Electron microscope (TEM) experiments were performed on a Tecnai T20 electron microscope with an acceleration voltage of 200kV.

d) Thermal analysis
Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) studied were performed on a Perkin Elmer instrument from 30 ˚C to 800 ˚C at heating rate of 25 ˚C/min.

4. Result and Discussion

4.1 FTIR

The FTIR spectrums of nHAp/GA composite are shown in Figure (1). The peak observed around 3389.13cm^{-1} is due to presence of –OH bond. This peak is mainly due to O-H stretching vibration in HAp. The peak at 1036.67cm^{-1} associated with the stretching modes of the P-O bonds of HAp. The peaks 662.71cm^{-1} and 565.03cm^{-1} are due to bending modes of P-O bonds in phosphate group. Thus, the presence of PO_4^{3-} group in HAp is almost confirmed from the IR studies. Carbonate anion derived band are also observed at 1454.05$cm^{-1}$and 1405.15cm^{-1}.

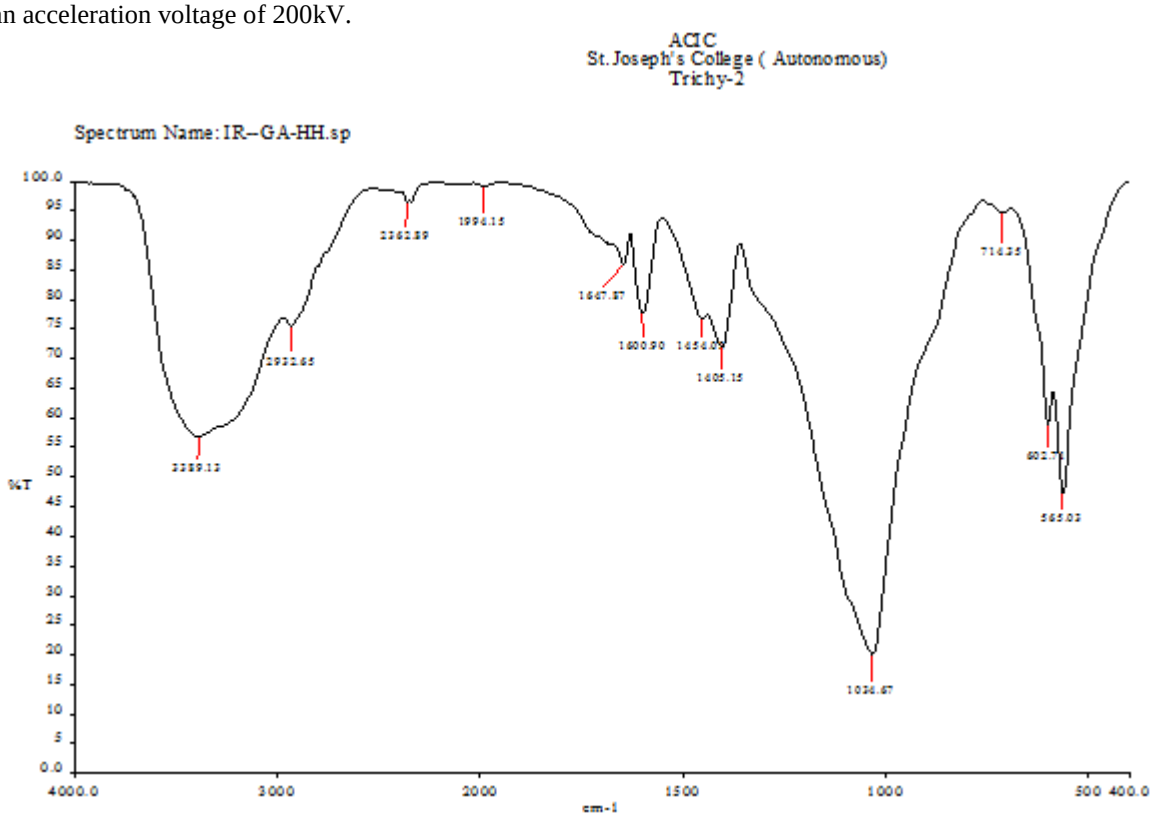

Figure 1: FTIR Spectrum of HAp/GA nano composite

4.2 XRD

The XRD patterns of nHAp/GA composite were taken. The patterns indicate the presence of crystallineHAp. The broad peak reveal that the particles size are very small range. The reflection planes corresponding to the characteristic XRD spectral peaks of HAp/GA composite are showm in fig(2). The observed Diffraction peaks are identified by standard JCPDS file no (09-0432). High intensitiy peaks at (002) (211) (300) confirm the nanosize and crystalline nature of sample.

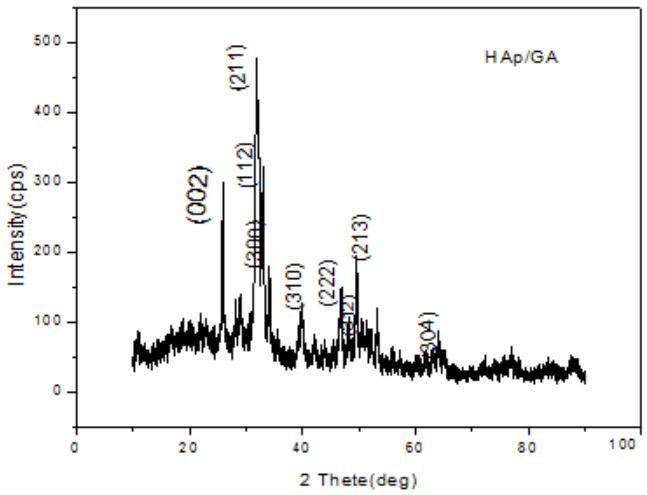

Figure 2: XRD Spectrum for nHAp/GA.

The crystallite size of HAp/GA is determined using the Scherrer formula [8]

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad \text{--- (1)}$$

Where, D is the crystallite size calculated for the (h k l) reflection, λ the wave length of CuKα radiation, β the full width of the peak at half of the maximum intensity and θ the diffraction angle of the corresponding reflection.

The lattice parameters are calculated based on the relationship between lattice spacing (d) and lattice parameters (a,c) of the hexagonal structure, expressed as

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{-- (2)}$$

The Fraction of Crystallinity (X_c) of the HAp/GA nanoparticles are calculated from the equation.[9]

$$X_C = \left(\frac{0.24}{\beta}\right)^3 \quad \text{--- (3)}$$

Specific surface area of the HAp/GAis determined by the formula

$$S = \frac{6\times10^3}{d\rho} \quad \text{--- (4)}$$

Where ρ is the crystallite Size (nm) and d is the theoretical density of HAp (3.16 g/cm^3).
The micro strain (ε) is calculated using the relation.[10]

$$(\varepsilon) = \frac{\beta\ cos\theta}{4} \quad \text{---- (5)}$$

The value of dislocation density (δ) is calculated using the relation.

$$(\delta) = \frac{1}{D^2} \quad \text{---- (6)}$$

The u-parameter valueiscalculated using the relation.[11]

$$u = \left(\frac{a^2}{3c^2}\right) - 0.25 \quad \text{--- (7)}$$

The unit cell volume (V) is determined by the relation.[12]

$$v = 0.865a^2c \quad \text{--- (8)}$$

The standard lattice constant a = 9.418 Å and c = 6.884 Å (JCPDS card no.09-0432) for the HAp has been matched well with the obtained values a = 9.370 Å and c = 6.889Å.

Unit cell volume and u parameters values are 523.180(Å)^3 and 0.3829.

Crystallite size, Fraction of Crystallinity, specific surface area, dislocation density, microstrain values are given table 1 and 2.

Table 1:2θ, FWHM, Miller induces value and Crystallize Size for nHAp/GA.

2θ	FWHM	h k l	Crystal size (nm)
25.869	0.211	0 0 2	6.7399
31.928	0.48	2 1 1	3.0034
49.54	0.33	2 1 3	4.6260

Table 2: Specific surface area, Micro Strain and dislocation density, Fraction Crystallinity for nHAp/GA.

Specific surface area(m^2/g)	Micro strain($10^{-3}lin^2m^{-4}$)	Dislocation density(10^{-15} lin/m^2)	Fraction of crystallinity
281.71	0.0514	0.0220	1.4715
632.19	0.1153	0.1108	0.125
410.44	0.0749	0.0467	0.3846

4.3 TEM

The morpology, particle size and pores have been investigated through TEM analysis. Figure 3(a)(b)(c) shows the TEM image of HAp/GA powder. The micrographs reveal the formation of rod-like shaped morphology of the particles in the powder sample. At room temperture, the powder sample consists of rod-like particles with length in the range 160 – 247nm. The existence of pores and their disordered arrangement were displayed in the figure.Although it was not possible to calculate the exact pore size from TEM image due to the low resolution. SAED pattern are shown in figure (4). SAED of the precipitates shows diffraction ring of patterns, which implies that the precipitates are crystalline in nature. This is agreed with XRD result and confirmed the nanosize componentts of nHAp/GA nanocomposite.

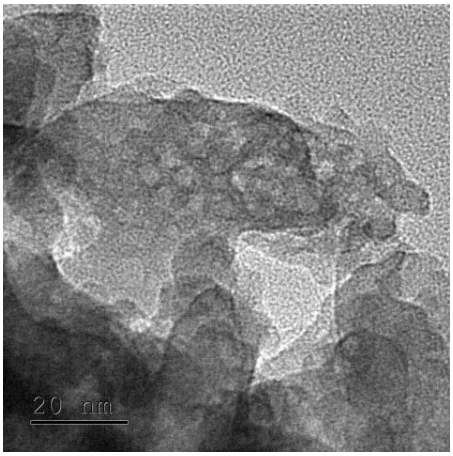

Figure 3:(a) TEM image for 20nm.

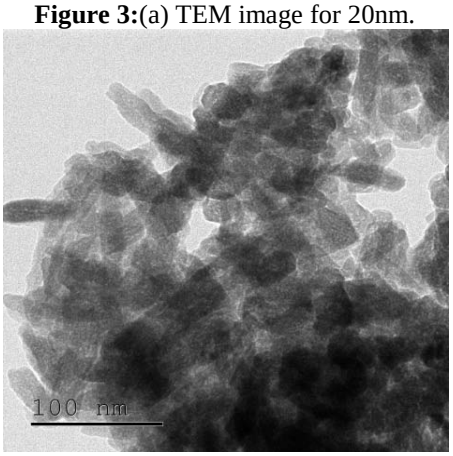

Figure 3(b): TEM image for 100nm.

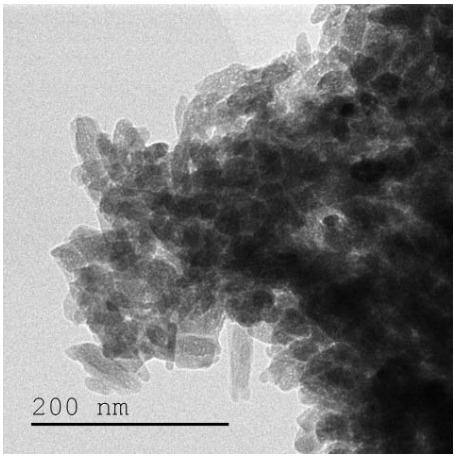

Figure 3(c): TEM image for 200nm

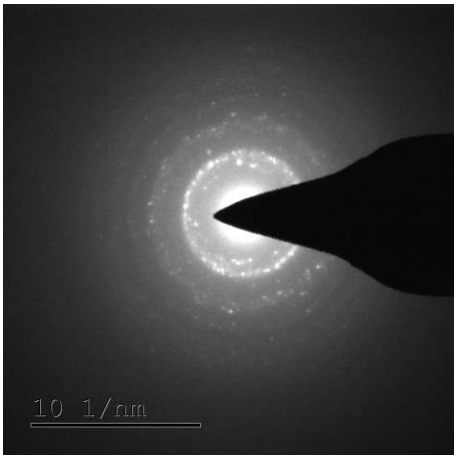

Figure 4: SAED pattern for nHAp/GA nanocomposite

4.4 Thermal analysis

The decomposition behavior of nanoHAp/GA composite is shown in fig(5). The nanoHAp/GA is calculated from the residual weight in TGA curves at 600˚C. However, since it is very difficult to control adsorbed water content in the composite, this nanoHAp/GA content is only an approximate value. A small decrease in weight, is associated with adsorbed water-removing when heated above 90˚C. The quick weight loss is observed from about 280˚C to 600˚Candbeyond 600˚C to 800°C no significant wt.loss was observed. The stable curve was noticed within this temperature range, which indicates thermal stability of HAp/GA powder. DTA curves shows endothermic peaks at 330˚C which are due to thermal degradation.

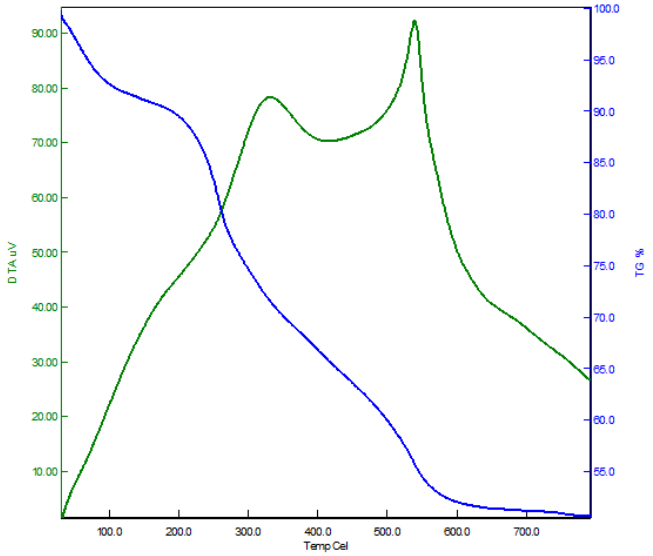

Figure 5: TG/DTA for HAp/GA nano composite

5. Conclusion

nHAp/GA composite were synthesized by modified wet chemical method. At room temperature and characterized by powder XRD, FTIR, TG/DTA and TEM. FTIR result conforms functional group like(O-H),(P-O),(C-O). The XRD, SAED patterns conform that hydroxyapatite has nano size of crystalline nature of the sample. TEM result suggests that the stoichiometric nHAp/GA exhibit particle with nanorod like morphology. SAED pattern are in good

Agreement with XRD Thermal properties of the material are assigned by TG/DTA analysis.The crystallite size, lattice parameters, specific surface area , volume density, micro strain, u parameter and dislocation density also measured by using XRD data. Nano materials are greatly promising in the development of more valuable orthopedic and dental implants. The result indicated that the composite material was expected to find application for bone repairing.

6. Acknowledgements

The Management of UrumuDhanalakshmi College, Tiruchirappalli forproviding research facilities in the campus.

References

[1] J.Fanghanel, T.Gedrange, P.Proff.Biomed Tech(Berl), 2008; 53(5),215-219.
[2] S.K. Biswal, U.K Parida and B.K Bindhani. “ Gold Nanoparticles capped with Tamarind Seed Polysacharide blended with Chitosan composite for the growth of phosphate Mineral”. IJCET. Vol.3,No.3(August 2013).
[3] Anjuvansingh, “ Hydroxyapatite, a biomaterial: Its chemical synthesis, characterization and study of biocompatibility prepared from shell of garden snail,Helixaspersa”, Bull.Mater. Sci., Vol.35,No.6, November 2012,pp 1031-1038.
[4] C.P Dhanalakshmi, L. Vijayalakshmi and V. Narayanan.“ Synthesis and characterization of

FHAp/CHITOSAN Nanocomposite and its Biomedical Application". International journal of nano and material Sciences, 2012,1(2):81-96.

[5] Christian sanchez, Denis Renard, Paul Robert, Chritstophe Schmitt, Jacques Lefebvre. "Structure and rheological properties of acacia gum dispersions". Food Hydrocolloids 16 (2002) 257-267.

[6] Badreldin H. Ali, AmalZiada, Gerald Blunden. " Biological effects of gum Arabic: A review of some recent research" Food and Chemical Toxicology47(2009)1-8.

[7] Ashwi MurugapanChockalingam, HemanKumaRamiya Ramesh Babu, RaghuramanChittor Jai PrakashTiwari. "Gum Arabic modified Fe_3O_4 nanoparticles cross linked with collagen for isolation of bacteria". Journal of Nanobiotechnology 2010,8:30.

[8] M.Rajkumar, N.MeenakshiSundaram, V. Rajendran. "Preparation of size controlled, stoichiometric and bioresorbable hydroxyapatite nanorod by varying initial pH, Ca/P ration and sintering temperature". Digest journal of Nanomaterials and Biostructures, vol.6, No 1, January-march 2011,p.169-179.

[9] R. Palanivel, A.Rubakumar. "Synthesis and spectroscopic characterization of hydroxyapatite by Sol-Gel method". International Journal of Chem Tech Research CODEN (USA):IJCRGG, Oct-Dec 2013, Vol.5, No.6, pp 2965-2969.

[10] M. Jothibas, C.Manoharan, S.Dhanapandian and S. Johnson Jeyakumar. "Influence of precursor concentration on sprayed In_2O_3 Thin Flims". Asian journal of chemistry; Vol.25, Supplementary Issue (2013), S59-S64.

[11] G.Vijayaprasath. G.Ravi, M.R. Manikandan, M. Arivanahan, M.Navaneethan and Y.Hayakawa. "A Comparative study on pure and Mg Doped Zno Nano structured Thin Films". Asian journal of chemistry; Vol.25, Supplementary Issue (2013), S258-S260.

[12] G.A. Gamal, F.A. Al-Mufadi, A.H. Said. "Effect of Iron Additives on the Microstructure of Hydroxyapatite". Engineering,Technology & Applied Science Research, vol. 3, No. 6, 2013, 532-539.

Author Profile

K. Senthilarasan, Research Scholar, Department of Physics, Urumu Dhanalakshmi college, Kattur, Trichirappalli, India

P. Sakthivel, Associate Professor. Department of Physics, Urumu Dhanalakshmi college, Kattur, Trichirappalli, India