

Development of Hydroxyapatite-Titania Composite for Implant Application

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF TECHNOLOGY

IN

BIOMEDICAL ENGINEERING

By

ANURAG RATHORE

(Roll No. 213BM1015)

Under the Guidance of

Dr. AMIT BISWAS



**Department of Biotechnology & Medical Engineering
National Institute of Technology Rourkela,
ORISSA-769008**

2015



DEPARTMENT OF BIOTECHNOLOGY & MEDICAL ENGINEERING

National Institute of Technology,

Rourkela-769008

CERTIFICATE

This is to certify that the report entitled “**Development of Hydroxyapatite- Titania composite for implant application**” being submitted by **ANURAG RATHORE** towards the fulfilment of the requirement for the degree of Master of Technology in Biomedical Engineering at Department of Biotechnology & Medical Engineering, NIT Rourkela is a record of bonafide work carried out by him under my guidance and supervision.

Dr. AMIT BISWAS

Dept. of Biotechnology and Medical Engg.
National Institute of Technology, Rourkela

ACKNOWLEDGEMENT

I feel immense pleasure and privilege to express my deep sense of gratitude, indebtedness and thankfulness towards all those people who have helped, inspired and encouraged me during the preparation of this report.

I would like to thank Dr. Amit Biswas, who provided me this opportunity to highlight the key aspects of an upcoming technology and guided me during the project work preparation, I would also like to thank Prof. Krishna Pramanik head of department (BM), Prof. S.K.Pratihar (CR) and Mr. L.K. Mohanty (CR) for their support and coordination.

I would like to thank whole heartedly my parents, family members whose love and unconditional support, both on academic and personal front, enabled me to see the light of this day.

Last but not the least, I would also like to thank my seniors Ms. Varshini, Sahely, Pinky, Dinesh, Puneet kumar and Nilardi N. Panda and my friends Rohan, Trupti and Ram for their kind support and helping behaviour.

Thanking you,

ANURAG RATHORE
213BM1015

Dept. of Biotechnology and Medical Engineering
National Institute of Technology, Rourkela

CONTENTS

Certificate	ii
Acknowledgement	iii
List of Figures	vi
List of tables	vii
Nomenclature	viii
Abbreviations	ix
Abstract	x

Chapter No	Title	Page No
1	Introduction	1
2	Literature Review	4
	2.1 Hydroxyapatite	5
	2.2 HAp composites	5
	2.2.1 HAp Zirconia composite	6
	2.2.2 HAp Alumina composite	6
	2.2.3 HAp Glass ceramics composite	6
	2.2.4 HAp Titania composite	7
3	Materials and Methods	9
	3.1 Experimental procedure	10
	3.1.1 Synthesis of HAp	10
	3.1.2 Pot milling	11
	3.1.3 Binder solution preparation	11
	3.1.4 compaction	12
	3.1.5 Sintering	12
	3.2 Characterization techniques	13
	3.2.1 Morphology and elemental analysis	13
	3.2.2 Dynamic light scattering	13
	3.2.3 X-ray diffraction analysis	13
	3.2.4 Fourier transform infrared spectroscopy	14
	3.2.5 Mechanical strength measurement	14

	3.2.6 Density and porosity measurement	14
4	Result and Discussions	16
	4.1 Particle size analyser	17
	4.2 Effect of sintering temperature on density and porosity	18
	4.3 Morphology analysis	20
	4.4 XRD analysis	21
	4.5 FTIR analysis	25
	4.6 Compressive strength	26
5	Conclusion	28
	5.1 Conclusion	29
	Future Scope	30
	References	31

LIST OF FIGURES

Figure No	Name	Page No
1	Flow chart of work plan	8
2	Flow chart for HAp synthesis	10
3	Size distribution by intensity obtained from DLS for HAp	17
4	Size distribution by intensity obtained from DLS for TiO ₂	18
5	Density of HAp- TiO ₂ composite	19
6	Porosity of HAp- TiO ₂ composite	19
7	SEM micrographs for HAp and HAp- Titania composite	20
8	XRD spectra of HAp sample	21
9	XRD spectra of HAp- Titania composite containing 5% Titania	22
10	XRD spectra of HAp- Titania composites 5%, 10% and 15% Titania	23
11	FTIR spectra of HAp and HAp- TiO ₂ composites	25

LIST OF TABLES

Table No	Name	Page No
1	Compressive strength of HAp- TiO ₂ composite	26

NOMENCLATURE

Sample name	Definition
5- 1h	HAp- Titania sample containing 5% Titania sintered for 1 hour at 800° C
5- 2h	HAp- Titania sample containing 5% Titania sintered for 2 hour at 800° C
5- 3h	HAp- Titania sample containing 5% Titania sintered for 3 hour at 800° C
10- 1h	HAp- Titania sample containing 10% Titania sintered for 1 hour at 800° C
10- 2h	HAp- Titania sample containing 10% Titania sintered for 2 hour at 800° C
10- 3h	HAp- Titania sample containing 10% Titania sintered for 3 hour at 800° C
15- 1h	HAp- Titania sample containing 15% Titania sintered for 1 hour at 800° C
15- 2h	HAp- Titania sample containing 15% Titania sintered for 2 hour at 800° C
15- 3h	HAp- Titania sample containing 15% Titania sintered for 3 hour at 800° C

ABBREVIATIONS

Name	Full form
HAp	Hydroxyapatite
TiO ₂	Titanium dioxide
H ₃ PO ₄	Phosphoric acid
HCl	Hydrochloric acid
Ca(OH) ₂	Calcium hydroxide
NH ₄ OH	Ammonium hydroxide
Zr	Zirconia
Al ₂ O ₃	Alumina
°C	Unit of temperature in degree centigrade
gm	Gram, unit of mass
RPM	Revolution per minute
MPa	Mega Pascal
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
EDS	Energy dispersive X- ray spectroscopy
DLS	Dynamic light scattering

Abstract

Hydroxyapatite is one of the defined bioactive materials. It is a potential candidate ceramic for bone and dental implants since it owns a superior biocompatibility. Due to its brittleness and poor mechanical strength, application of HAp is limited at load bearing site. Various routes have been investigated for improving the mechanical properties of hydroxyapatite. Recent studies show various HAp composites were fabricated to improve mechanical strength. Titanium dioxide has very good biocompatibility. Titanium dioxide also promotes cell growth and proliferation. Titanium dioxide is added in different weight percentages i.e. 5%, 10%, 15% in to HAp. Samples were sintered for different time at 800°C. Developed composite were further characterized for morphology, phase, functional group analysis and compressive strength. It was found that HAp- Titania composite containing 10% Titania has better compressive strength 59.8 MPa with 20-40% porosity than any other developed composite of selected composition.

Keywords- Hydroxyapatite, biocompatibility, sintering process, compressive strength

CHAPTER 1

INTRODUCTION

1.1 Introduction

Composite or compositional materials are made up of two or more materials having different physical and chemical properties. Composite materials have different properties than individual constituent materials. Within composite materials, one can easily distinguish the constituent materials; they do not dissolve with each other. Composite materials are very light in weight and provide good strength and stiffness [1].

Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is one of the inorganic minerals present in human bone. It has various applications in orthopaedics and dental implants due to its great bioactivity [2]. HAp is basis materials of apatite, which are found as main component in bone and teeth [3]. Hydroxyapatite composite can also be used as bone fillers because it generally shows good osteoconductivity. One more important thing about HAp is its close resemblance with human bone. Various implants are made up of stainless steel, titanium and its alloy, for improving bone ingrowth, coating of HAp is done over the implant which also makes it bioactive [4]. HAp is also used for increasing stability and strength of scaffolds. There are many application of HAp; however HAp cannot be used at load bearing sites because of its poor mechanical strength and brittleness. Over the last decade various composite materials of HAp were fabricated to improve its mechanical strength. HAp shows good bone bonding ability towards earlier new bone apposition. For utilising this property, HAp and alumina composite was fabricated to improve mechanical strength [5]. Bioactive glass and HAp composite is also suitable for coating over metallic implants [6]. We can improve mechanical strength of HAp by making its composites with ZrO_2 , TiO_2 , Al_2O_3 , and Si_3N_4 . HAp and zirconia composite was fabricated because zirconia has high mechanical strength and nontoxic [7].

Various studies show that HAp and Titania composite presents balanced combination of good functionally graded bioactive material [8].

In the present work hydroxyapatite and Titania composite have been fabricated by powder metallurgy route. The different percentages of TiO₂ have been taken to improve the mechanical strength and biocompatibility of the developed composite as TiO₂ has very good biocompatibility. Titanium dioxide also promotes cell growth and proliferation. By mixing TiO₂, young modulus can also be increased [9]. The characterizations of the composite have been done for its density, porosity, morphology, phases and mechanical strength.

CHAPTER 2
LITERATURE REVIEW

2.1 Hydroxyapatite

Hydroxyapatite is one of the defined bioactive materials. It is the major constituents of natural bone and teeth. It has high biocompatibility and osseointegration property. The chemical formulae is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Hydroxyapatite is a member of apatite group that contains hydroxyl group. One of the major drawbacks of HAp is low mechanical strength [2-5].

HAp can be synthesized by various methods like wet chemical method, precipitation and it can be directly extracted from bovine bones (bio waste).

Calcination of HAp powder is generally done at temperature below 800°C . At high temperature, dehydroxylation of HAp will occur and it decomposes into tri calcium phosphate which has higher dissolution rate [6].

Mechanical properties of synthesized HAp are basically depend on the starting materials. Rao et al showed in their report that compressive strength of HAp within the range 17.8- 207 MPa. Basically they took CaCO_3 and H_3PO_4 as starting materials [7]. One another important parameter is responsible for compressive strength is porosity. Higher porosity causes poor mechanical properties. It is possible to produce HAp at low temperature but due to production of HAp monoliths, poor mechanical properties are achieved. Compressive strength are reported within a range of 34- 51 MPa [8]. Compressive strength of cortical bone is 130 MPa in longitudinal loading and 50 MPa in transverse loading. Human mandible is the longest and strongest bone in face. Its compressive strength lies within a range 0.22-10.44 MPa with mean value of 3.9 MPa [9].

2.2 HAp composites

Many researches was done on HAp composites in some past year, as mechanical strength of HAp is not so good to use at load bearing sites. To overcome this problem various HAp

composites were fabricated. Recent studies show that composite of ZrO_2 , glass ceramics, TiO_2 , Si_3N_4 with HAp have improved mechanical strength [11]. Among the different developed HAp composite some of them are discussed here.

2.2.1 Hydroxyapatite- zirconia composite

Zirconia is an inorganic material having low toxicity and high mechanical strength. It shows various applications in hip prosthesis, dental implants. Mechanical strength of zirconia after sintering is higher enough in comparison with cortical bone. When bonding occurs with host bone stress shielding will take place and some fracture will occurs. Zirconia also has very low affinity to cell and tissue. These problems can be solved by fabricating HAp- ZrO_2 composite as this micro porous composite may improve these properties. But according to many research composite material still showed higher mechanical properties than cortical bone [3].

2.2.2 Hydroxyapatite– alumina composite

Alumina is bioinert material towards human tissues which makes him promising material to make composite with HAp. It also has high mechanical strength. But there is a chance with alumina incorporation is that mechanical strength may improve but we may compromise with biocompatibility. In HAp- Alumina composite higher compressive strength and flexural strength may be achieved. Alumina addition may effect strengthening. Higher alumina content causes decomposition of HAp. One another drawback with this composite is lack of chemical bonding between sintered alumina and tissue, so biocompatibility of this composite is not up to the mark [11].

2.2.3 Hydroxyapatite glass ceramics composite

Bio glass ceramics and their composite are used to fabricate porous scaffolds, dense scaffolds and porous bone filler materials. According to recent studies, release of zinc from an implant material may play an important role in bone formation around the implant. Zinc can connect

to osteoblastic cell and promote renewal of bone. This property of zinc is called antimicrobial property. Other bioactive glasses such as B_2O_3 , TiO_2 show good bioactivity [10].

Bioceramics may also fabricate with HAp and additives of silica. Excess silica promotes grain growth and crystallinity, this composite is called HAP+TCP bio glass. This composite promotes bone like layer growth much faster than pure HAp [14].

2.2.4 Hydroxyapatite- TiO_2 composite

Titanium has high bio affinity and good mechanical strength. Research was done on the HAp and Titania composite in recent years because of its favourable biocompatibility. Titanium and Titania may be useful as reinforcing phase in HAp based composites [15]. HAp- TiO_2 composite may be an ideal photo catalyst due to its prominent properties such as chemical stability, high light damaging resistance. It has very high activity for photo oxidation of organic compounds. It is proved that it can remove organic compound. Nonami et al reported that this composite can be used for air purification. This composite may play an important role to control environmental pollutions [16].

As per the above discussion various HAp composites may be fabricated. In some composites there are some drawbacks like in case of alumina we may get the desired strength but there is an issue of biocompatibility. Zirconia provides higher strength that causes fracture in bone due to stress shielding. In these composite one of the major phenomenon occurs is transformation of HAP into TCP which has higher dissolution rate.

Objective

The objective of present study is to fabricate Hydroxyapatite- Titania composite by powder metallurgy route to improve mechanical strength.

Work plan

Following specific objectives have to be achieved.

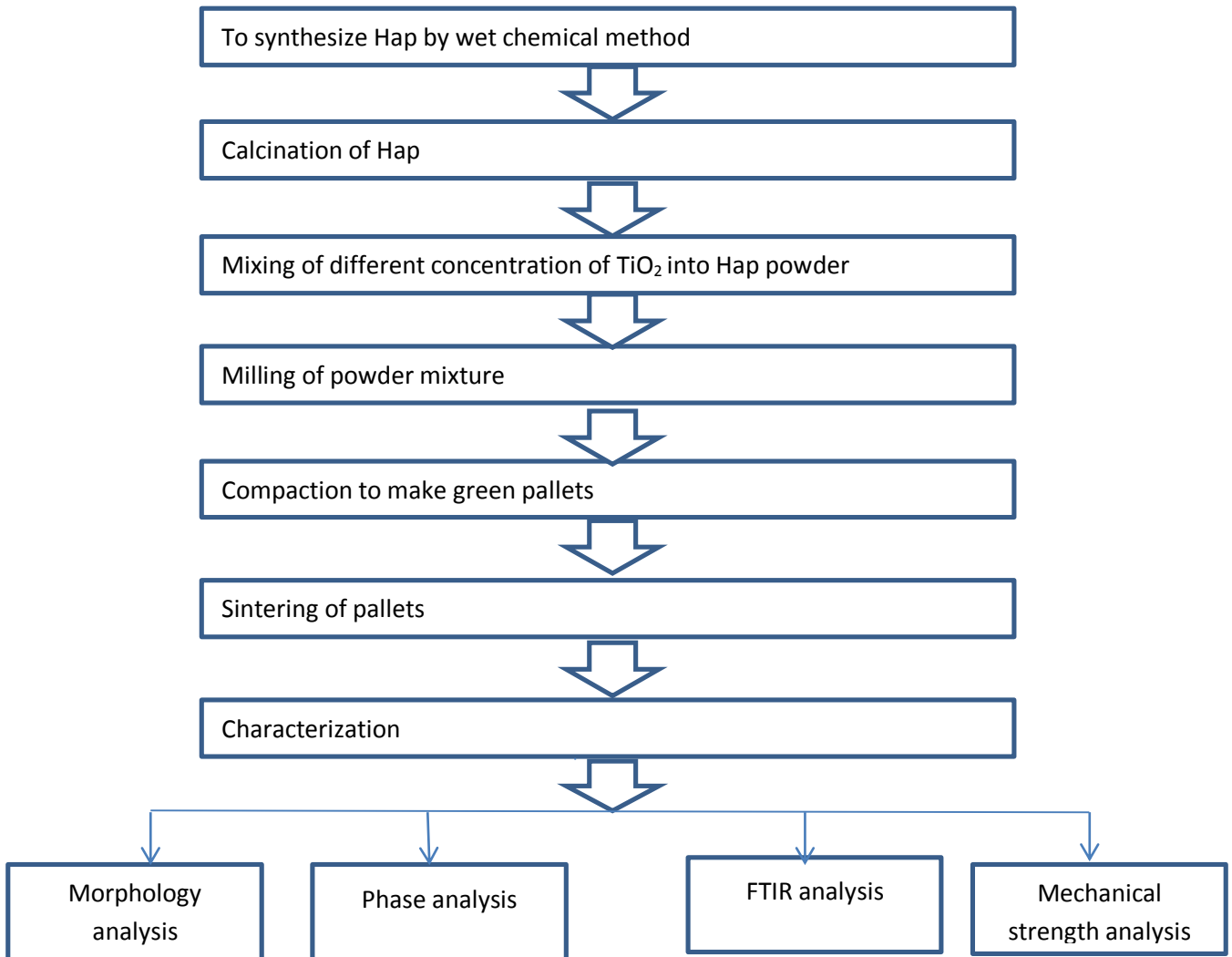


Figure 1 Flow chart of work plan

CHAPTER 3

MATERIALS AND METHODS

3.1 Experimental procedure

For fabrication of HAp- Titania composite, commercially available chemicals were used. Titanium dioxide was procured from qualigens fine chemicals. Hydroxyapatite was synthesized by wet chemical method.

3.1.1 Synthesis of HAp

For synthesizing HAp, commercially available laboratory grades chemicals were used. Calcium hydroxide ($\text{Ca}(\text{OH})_2$ (Merck)), ortho phosphoric acid (H_3PO_4 (Sigma- Aldrich)), Ammonium hydroxide (NH_4OH , (Rankem)), Hydrochloric acid (HCl , (Merck)) were taken as starting materials.

HAp was synthesized by wet chemical method. Following steps had been carried out for synthesizing HAp.

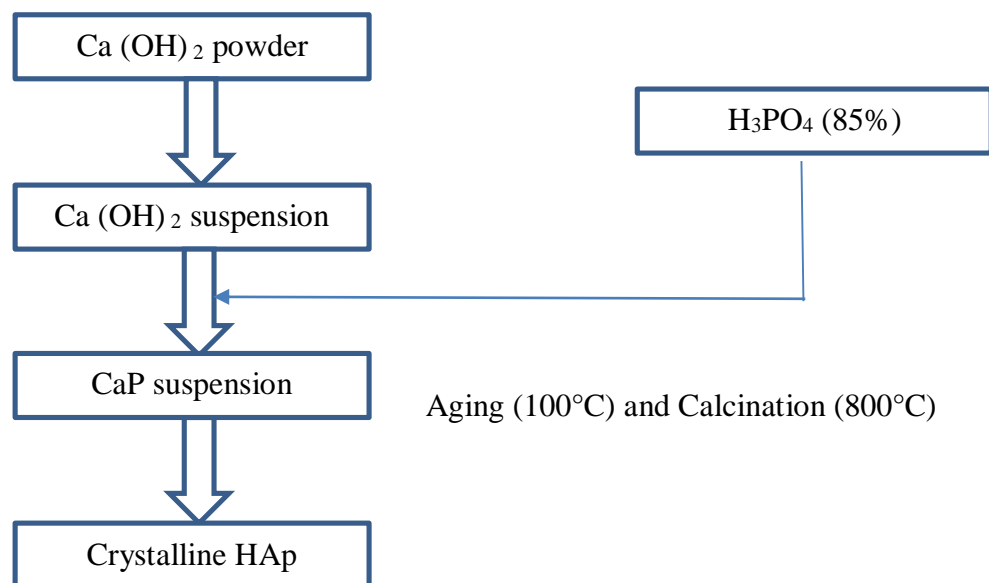


Figure 2 Flow chart for HAp synthesis

1. Calcium hydroxide, ortho phosphoric acid, ammonium hydroxide were taken as starting materials.

2. 0.284 mole (21.02gm) calcium hydroxide was added into 100 ml of water in a 500 ml beaker.
3. It was put on the magnetic stirrer for 1 h at 1000 RPM.
4. In the calcium hydroxide solution 8.79 ml of 85% orthophosphoric acid was added at a rate of 1.2 ml per minute. At the time adding pH is maintained at an accuracy of ± 2 .
5. Again this mixture was stirred vigorously for 24 h at 1000 RPM.
6. Add 0.28 mole NH_4OH to HAp slurry after 24 h to stabilize the pH above 9.
7. Aging was done at 100°C for 1 h.
8. Calcination was done at 800°C for 2 h to get compact (Crystalline) HAp.

Chemical reaction involved in synthesizing of HAp.



After calcination crystalline HAp will be formed. Now three different concentration of TiO_2 i.e. 5%, 10%, 15 % (Wt. %) was taken and added into HAp powder.

3.1.2 Pot milling

Pot milling (model no. JM6) was done to make powder finer. Powder was filled in plastic container and zirconia balls were inserted in this container. Here zirconia balls are used as grinding media. Now this container was kept fixed in a pot by using sponges, cottons. Pot was put on the rotating bars of this machine. Some parameters were taken into account like speed was measured and it was 70 RPM (approx.). 10 numbers of zirconia balls having 10 mm diameter were used. The machine was run for 30 minutes.

3.1.3 Binder solution preparation

4 % (w/v) PVA (Poly Vinyl Alcohol) binder solution was prepared. It was heated on a magnetic stirrer, simultaneously stirred. The weighed amount of PVA was added in small proportions, only when the previous addition had dissolved. It was ensured that the

temperature remained below 90°C. Usually, constant heating is not required and it was heated in intervals but continuously stirred. Sometimes extra water was also added to keep up the required percentage of water. Continuous stirring resulted in a clear transparent solution.

3.1.4 Compaction

Compaction was done by using automatic hydraulic press Model 3887, Carver Inc. USA. 13 mm diameter punch was used to make pallets. Firstly it was cleaned with acetone. It was again cleaned with stearic acid which acts as a lubricant. This process was repeated after each and every use. Sample was filled in the dye punch and compressed. Green pallets of 13 mm diameter and 3 mm height were formed by die pressing under a load of 5 ton with a dwell time of one minute.

3.1.5 Sintering

These pallets were sintered at 800°C for different time in normal atmosphere at 3°/min rise in temperature. Some samples from each composition were kept for 1 h, 2h and 3 h. Sintering was carried out at 800°C because above this temperature HAp decomposes into tri calcium phosphate which has higher dissolution rate.

The sintering temperature and time of heat treatment are the most important parameters influenced on HAp properties. During sintering, mainly two processes are taken place to affect the morphology of solid. These two processes are densification and grain growth. Both processes are thermally activated. Higher sintering temperature causes coarsening of HAp grains that deteriorate the properties of HAp. In step of sintering, expansion of powder is observed. Subsequently, in higher temperature compaction process is initiated. Finally the sample shrinks and reaches its maximum density in sintered form. Sintering is done to achieve the highest density while reducing grain growth.

3.2 Characterization techniques

3.2.1 Morphology and elemental analysis

SEM (scanning electron microscope (JEOL JSM 6480 LV)) is used for the check of surface morphology of the sample. EDS was performed for elemental analysis. In this type of electron microscope, images of the sample are scanned with the help of electrons. Electrons interact with the atoms and contain useful information about the sample's morphology, topography etc. At a voltage of 15 KV, samples were scanned at various magnifications.

Energy dispersive spectroscopy- in EDS, X-ray is used for the analysis of the sample. EDS has characterization capabilities because each element has a unique atomic structure allowing only unique set of peaks on its X-ray spectrum. In EDS, high energy particles are incident onto the surface of the sample. EDS tells about the chemical composition of the sample. EDS is used to reveal the elements present in the samples.

3.2.2 DLS (Dynamic light scattering)

DLS is a useful tool to determine the agglomeration state of nanoparticles as a function of time. It characterizes the size of a colloidal particle in a solution and measures the hydrodynamic size of a particle. Zetasizer particle size analyzer (Malvern nano ZS) performed it.

3.2.3 X-ray Diffraction analysis

X-ray diffraction is a versatile, non- destructive technique that extracts detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD analysis is usually based on the principle of constructive interference, i.e. when a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ , diffraction occurs only when the distance travelled by the rays reflected from consecutive planes differs by a number n of wavelengths. The composition of developed composite was analyzed using X-Ray diffractometer (Rigaku Japan Ultimate IV)

using Ca-K α radiation ($\lambda=0.1542 \text{ \AA}$). X-ray intensity was measured for angles in the range of $2\theta= 10$ to 70° for HAp and $2\theta= 03$ to 50° for HAP- Titania composite with scanning rate of 3° per minute and step size of 0.05.

3.2.4 Fourier transform infrared spectroscopy

Organic and inorganic compounds were identified by determining the molecular composition and functional groups by using Fourier transform infrared microscopy, the chemical composition of any sample can be easily determined by FTIR. Here it was done by using infrared microscope (Shimadzu, IR prestige 21). KBr was mixed in the HAp powder. Spectra were recorded over the range of wave number $350\text{-}7800 \text{ cm}^{-1}$.

3.2.5 Mechanical strength

Mechanical strength (compressive strength) was tested of pellets by using universal testing machine (H10 KS Tinius Olsen USA). Pellets diameter was 13 mm and height was 6 mm.

3.2.6 Density and porosity measurement

Density was measured using Archimedes principal. Dry weight was calculated. After that weight was calculated inside the water that is known as suspended weight. At last wet weight was taken. Using the following formulae we can calculate the density.

$$\text{Bulk density} = (D) / (W-S)$$

Where

D = dry weight

W = wet weight

S = suspended weight

Apparent porosity was calculated using the following formulae.

$$\text{Apparent porosity} = ((W-D) / (W-S)) * 100$$

Where

D = dry weight

W = wet weight

S = suspended weight

CHAPTER 4

RESULTS AND DISCUSSION

The HAp-titania composite was fabricated by powder metallurgy. The composite thus obtained are characterized for morphology, chemical composition, crystallographic structure, density, apparent porosity, mechanical strength and discussed in the following sections.

4.1 Particle size analyser

Size and shape is the key feature that governs the physical stability of TiO₂ nanoparticles, both in vivo and in vitro. The techniques that are generally employed for determination of mean particle size include DLS, TEM.

Figure 3 shows the particle size distribution by intensity obtained from DLS for pure hydroxyapatite.

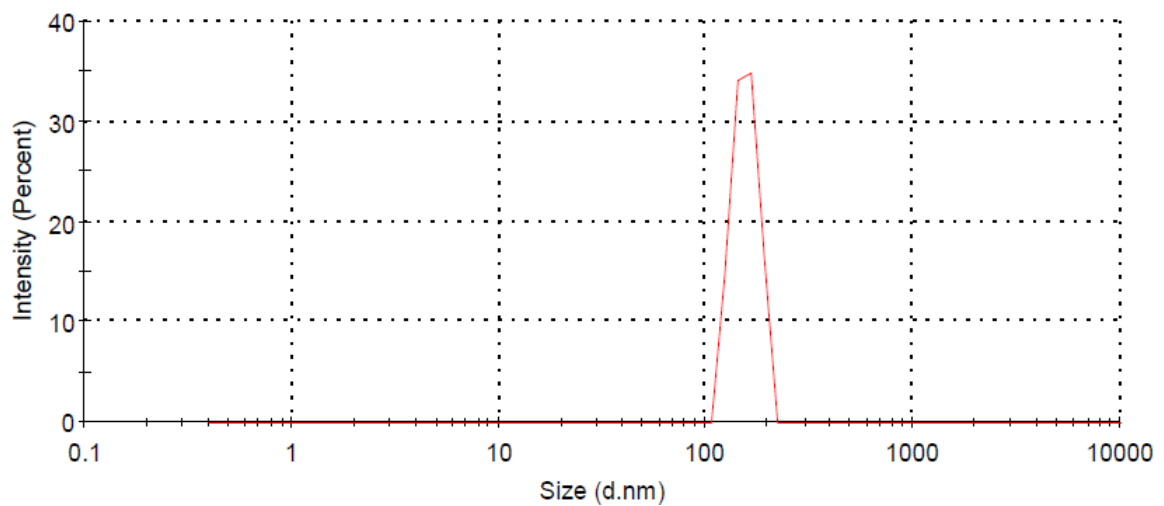


Figure 3 Size distribution by intensity obtained from DLS for HAp

The particle size of HAp was found in range within 100-400 nm with average particle size of 154.7 nm.

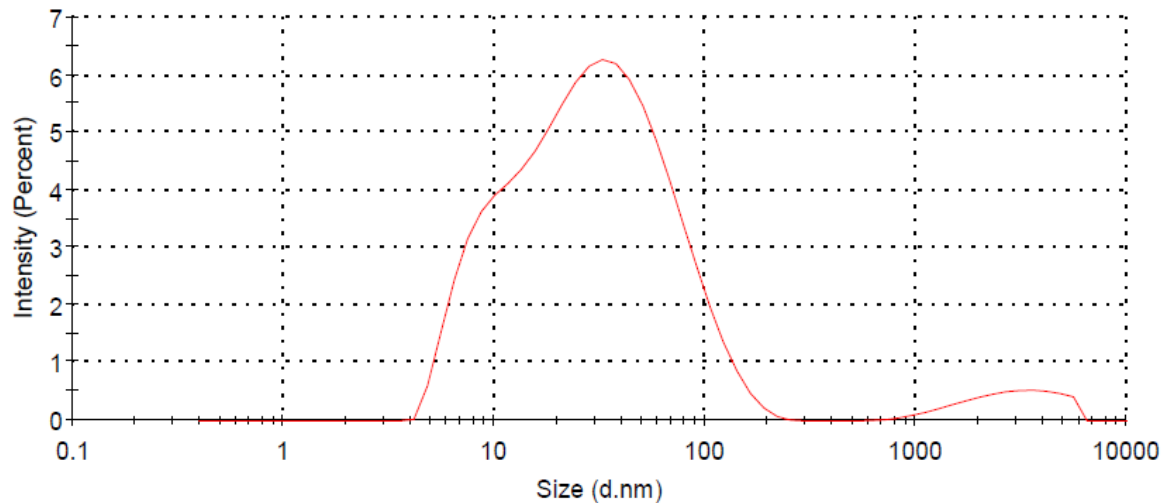


Figure 4 Size distribution by intensity obtained from DLS for TiO₂

Figure 4 shows the particle size distribution by intensity obtained from DLS for titanium dioxide. The particle size of titanium dioxide were found in the range within 4-200 nm and very less amount of intensity falls in the range of 1000-7000 nm with average particle size of 37.10 nm.

4.2 Effect of sintering time on density and apparent porosity of HAp-Titania composite

The density data of HAp composite with various content of TiO₂ are measured and it is plotted in Figure 5. This data was compared with theoretical data and found that densities of sintered samples are closer to theoretical data. The density of HAp is 3.06 g/cc. This indicates that either the occurrence of sintering temperature, leading to third phases or the presence of large porosity [15].

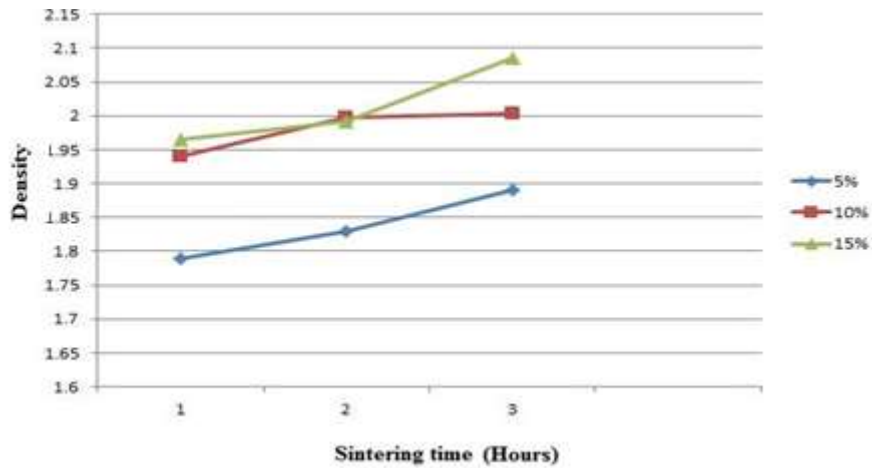


Figure 5 Density of HAp- TiO₂ composites

Density will be higher for higher sintering time. Sample will get compact in nature. HAp-Titania composite containing 15% Titania shows higher density at higher sintering time. The increase in density with addition of TiO₂ is due to the higher densities values of Ti/TiO₂ than HAp [15].

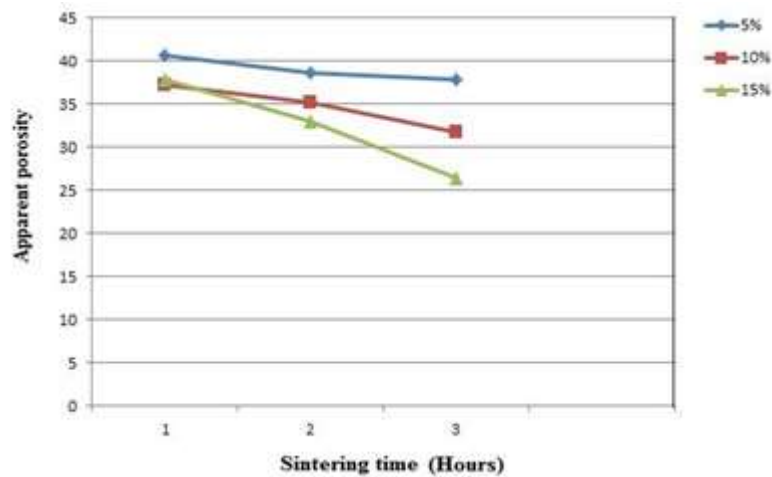


Figure 6 Porosity analysis of HAp- TiO₂ composites

Figure 6 shows the effect of sintering temperature on apparent porosity of developed HAp-Titania composite. Apparent porosity of the developed composite was determined and it was seen that porosity is less for higher sintering time, Porosity decreases as sintering time

increases. HAp- Titania composite containing 5% Titania has higher porosity and HAp- Titania composite containing 15% Titania has minimum porosity.

4.3 Morphology analysis

Figure 7 shows the SEM micrograph of the HAp and TiO₂-HAp composite.

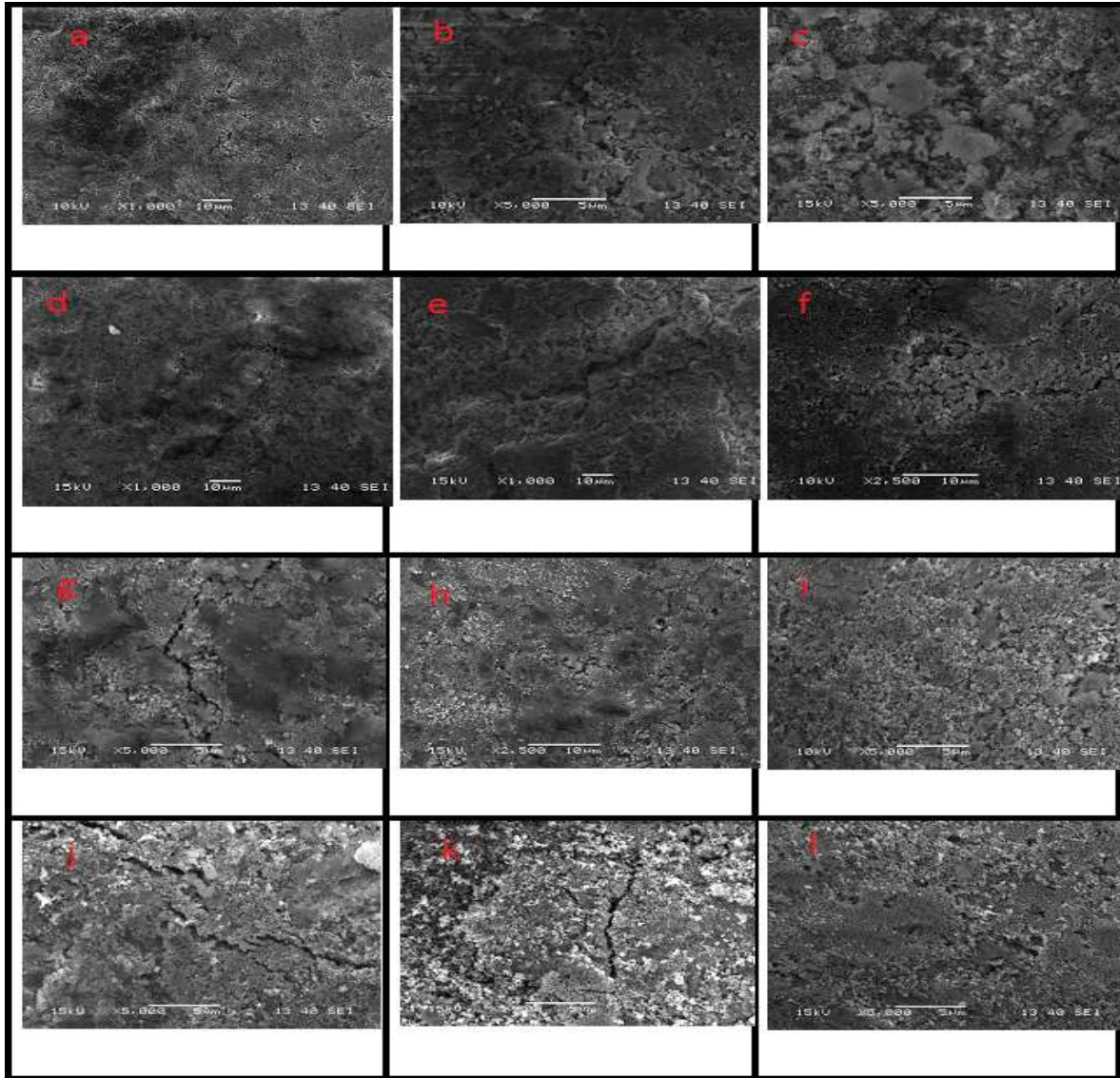


Figure 7 SEM micrograph of (a) HAp sample sintered for 1h. (b) HAp sample sintered for 2h. (c) HAp sample sintered for 3h. (d) 5- 1h sample (e) 5- 2h sample (f) 5- 3h sample (g) 10- 1h sample (h) 10- 2h sample (i) 10- 3h sample (j) 15- 1h sample (k) 15- 2h sample (l) 15- 3h sample

Figure.7 (c) shows the SEM micrographs of pure HAp sintered for 3 h, which is characterized by the dense microstructure with HAp particles of submicron size. It can be inferred from these images that HAp transformed into more dense and highly compact form. Figure7 (d), (e), (g), (h), (j) and (k) show the SEM micrographs for different weight percentages of Titania- HAp composites. Cracks are formed in samples for low sintering time (1h, 2h). The untransformed amorphous phase of HAp and Titania are responsible for the formation of cracks on the sample. The mismatch of coefficient of thermal expansion of this two phase occurs at the time of cooling also contribute to the crack formation. Cracks are not formed for higher sintering time, as it can be observed from Figure7 (i) and (l). Higher sintering time leads to the compaction of powder whose volume get increased when pass through 750°C [20]. This causes less chances of crack formation in the sample when the sintering time is 3h. In 10-3h and 15-3h HAp- Titania composites cracks are not observed and dense microstructure is obtained with finer HAp particles of submicron size.

4.4 XRD analysis of samples

The phase change was carried out by X-ray diffractometer. XRD pattern of sintered HAp and HAp- Titania composites are shown in the Figures 8 and 9 below. The peaks are compared with the standard JCPDS data file of HAp and Titanium dioxide.

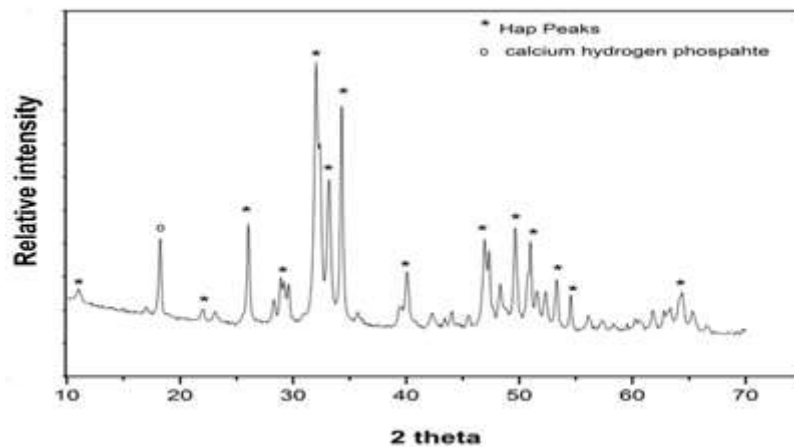


Figure 8 XRD spectra of pure sintered HAp sample

Figure 8 shows the XRD profile of sintered HAp sample, which was done at 800°C. The spectra obtained were compared with the standard data of HAp from JCPDS file (09-0432). Most prominent peaks were obtained at $2\Theta = 26.927, 32.483, 34.757, 36.611$ degree. One peak of calcium hydrogen phosphate was also found at 17.546 degree. The powder consists of mainly the HAp with small amount of calcium hydrogen phosphate as reveals from few low intensity peaks in the XRD profile. HAp starts decompose only above 800° C into bicalcium phosphate [18]. Therefore no such peaks of BCP and TCP are observed in the HAp sample.

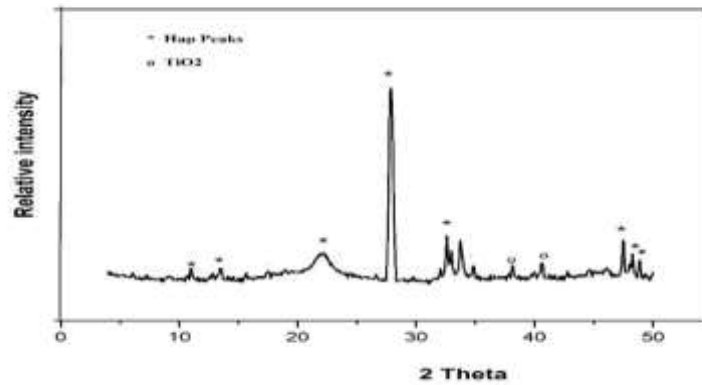


Figure 9 (a) XRD spectra of sintered 5- 1h sample

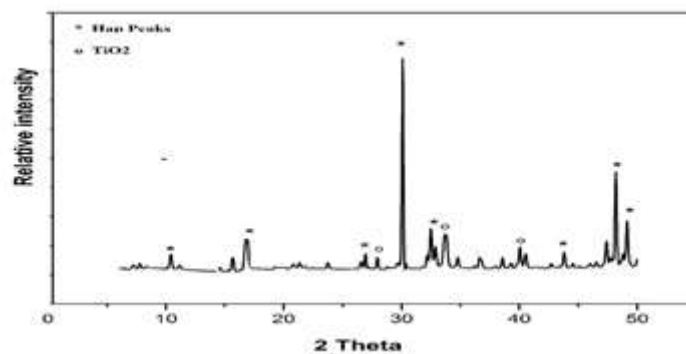


Figure 9 (b) XRD spectra of sintered 5- 2h sample

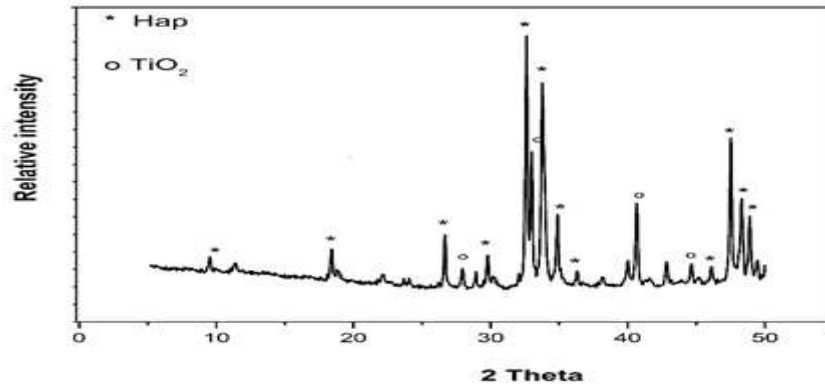


Figure 9 (c) XRD spectra of sintered 5- 3h sample

Figures 9 (a), (b) and (c) show the XRD profile of the HAp-TiO₂ composite having 5% TiO₂ sintering for 1h, 2h and 3h respectively. Presences of HAp, titanium dioxide were confirmed after analysis the different peaks formed in the XRD profile. The spectra were compared with the standard data. Peaks were matched with JCPDS file number of HAp (09-432) and Rutile (77-0442). Prominent peaks were found at $2\Theta = 30.087, 32.485, 48.713$ degree for HAp, $27.937, 39.305, 44.528$ degree for rutile. It can be easily confirmed by these XRD spectra that for low sintering time composite were little bit amorphous in nature. Crystalline behaviour increases for higher sintering time.

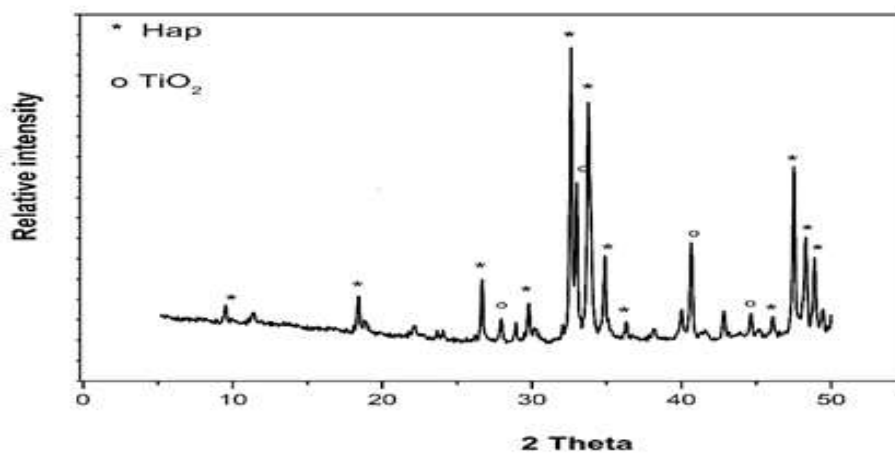


Figure 10 (a) XRD spectra of sintered 5- 3h sample

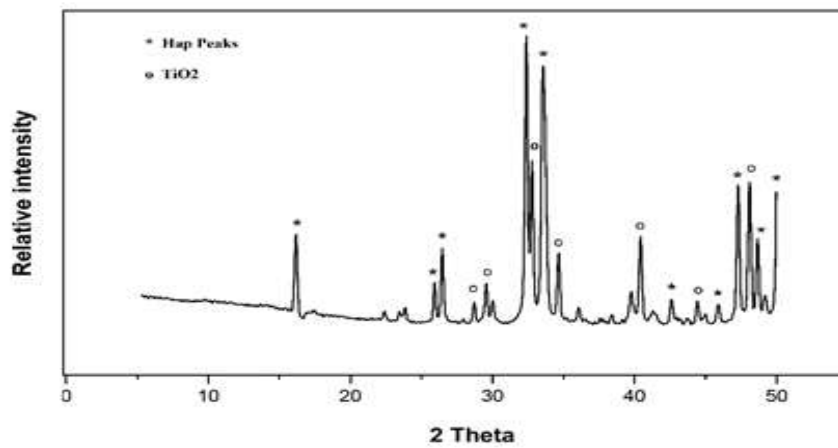


Figure 10 (b) XRD spectra of sintered 10- 3h sample

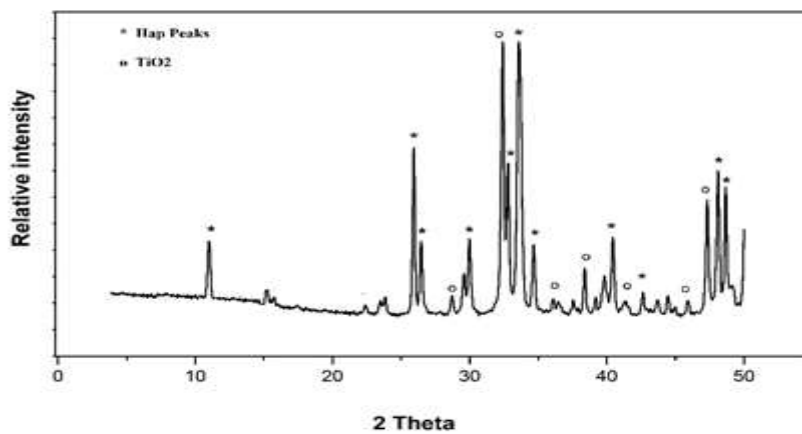


Figure 10 (c) XRD spectra of sintered 15- 3h sample

Figures 10(a), (b) and (c) show the XRD profile of the HAp-TiO₂ composite having 5% TiO₂, 10% TiO₂ and 15% TiO₂ sintering for 3h. Presence of HAp, titanium dioxide was confirmed after analysis the different peaks formed in the XRD profile. The spectra were compared with the standard data. Peaks were matched with JCPDS file number of HAp (09-432) and Rutile (77-0442). It can be inferred from the XRD spectra is that there are many peaks of TiO₂ with high intensity for higher weight percentage of TiO₂.

4.5 FTIR Analysis

The FTIR spectra of HAp and HAp reinforced TiO₂ composites are shown in Figures 11 (a), (b), (c) and (d). Vibrational and stretching bond of OH⁻ can be easily seen at 3571 cm⁻¹. As sintering time increases the intensity of this bond decreases. Phosphate group was found at 450-600 and 970 cm⁻¹. At 870 cm⁻¹ HPO₄²⁻ group was found. Since there is not a distinct band in the region of 1400-1600 cm⁻¹ that indicates that samples do not contain large amount of carbonate ions [15]. However HAp samples contains carbonate ions as there is a band at 1400-1450 cm⁻¹. The presence of rutile can be confirmed from the presence of Ti-O bands at 500-800 cm⁻¹ (broad peaks) [19]. Presence of HAp is also confirmed with XRD spectra.

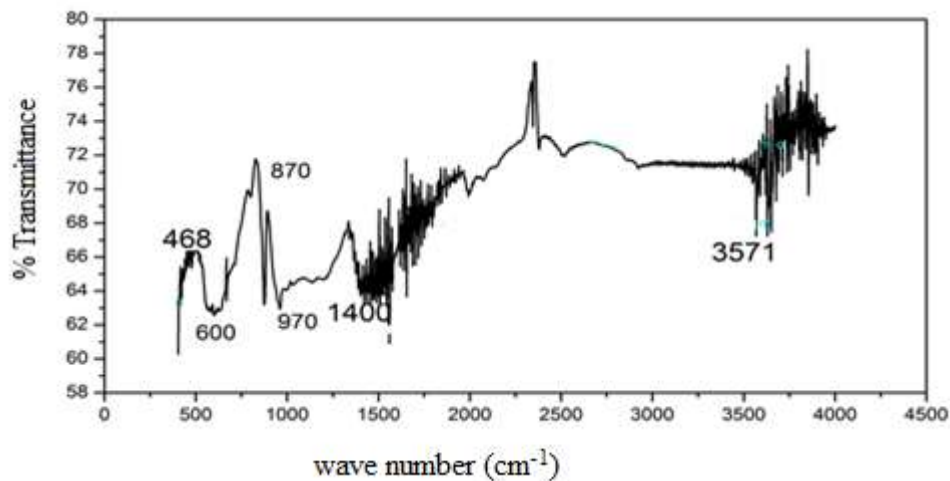


Figure 11 (a) FTIR spectra of HAp

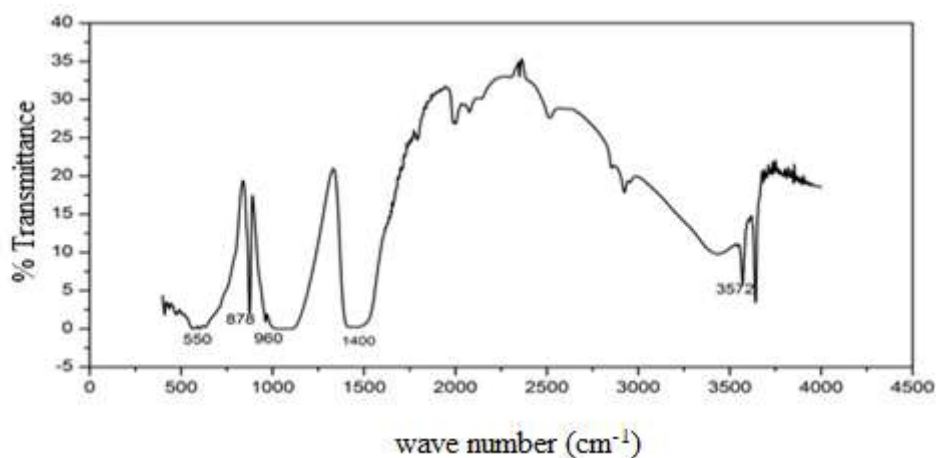


Figure 11 (b) FTIR spectra of HAp- Titania composite containing 5% Titania

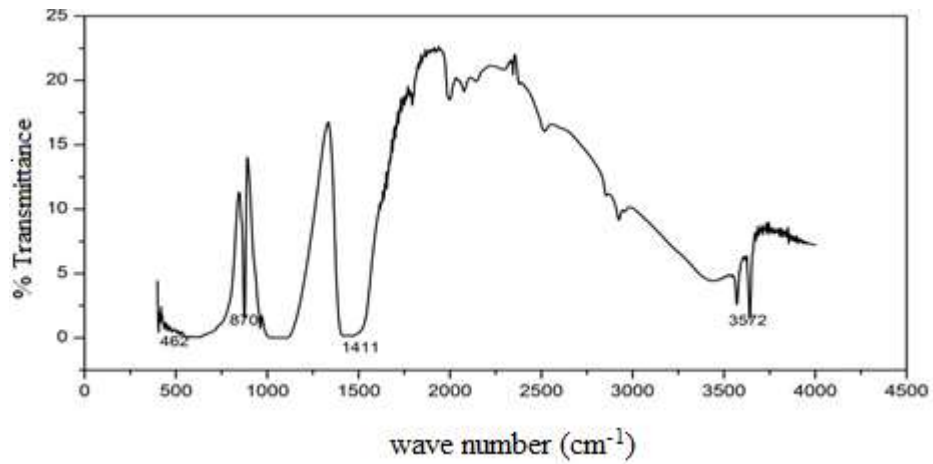


Figure 11 (c) FTIR spectra of HAp- Titania composite containing 10% Titania

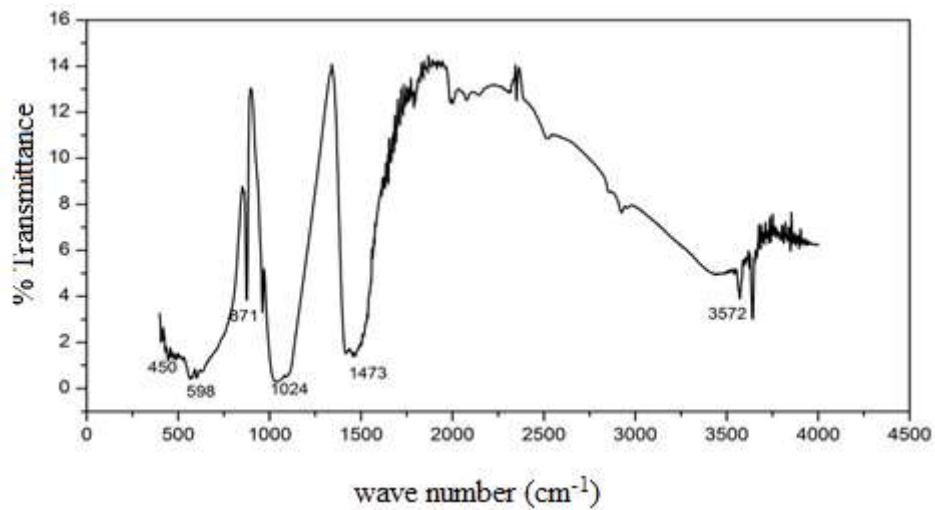


Figure 11 (d) FTIR spectra of HAp- Titania composite containing 15% Titania

4.6 Compressive strength

One sample from each composition was tested for compressive strength. The Table 1 shows the maximum force and compressive strength of respective samples.

Table 1 Compressive strength of HAp- Titania composite

Test	0% Titania	5% Titania	10% Titania	15% Titania
Maximum force	4253 N	7373 N	8040 N	6620 N
Compressive strength (MPa)	38.2	54.9	59.8	49.9

It can be inferred from here that HAp- Titania composites have good compressive strength having higher porosity. Since porosity is important factor to determine the strength of composite. Higher the porosity, lower the strength [7].

It is clearly observed that HAp- Titania composite containing 10% Titania shows better composite to have a maximum compressive strength 59.8 MPa among all the developed composite of selected composition.

CHAPTER 5

CONCLUSION

Conclusion

HAp- Titania composite with different weight percentages of Titania were fabricated by powder metallurgy route. Samples sintered for higher sintering time were found to be free from cracks. Samples were tested for compressive strength and it was found that compressive strength of HAp- TiO_2 composite is high enough than hydroxyapatite with 40% porosity. Among all different percentages of Titania in HAp- Titania composite, HAp- Titania composite containing 10% Titania has better compressive strength and it was 59.8 MPa. It is concluded that developed Titania- HAp composite has suitable materials for load bearing application.

Future scope

Biological characterization of developed composite can be done. Composite can be checked for biocompatibility, bioactivity and osseointegration. Oestrogenic activity of MSCs can be studied.

References

1. Wang M., *Biomaterials*, Volume 24, Issue 13, pp. 2133-2151
2. E. Mohseni, E. Zalnezhad, A.R. Bushroa, *International Journal of Adhesion & Adhesives* 48 (2014) 238–257
3. Takuya Junior Matsumotoa, Sang-Hyun Ana, Takuya Ishimoto, Takayoshi Nakanob, Takuya Matsumotoa, Satoshi Imazato, *Dental materials* 27(2011) e205–e212
4. Emilija Fidancevska, Gordana Ruseska, Joerg Bossert, Yuan-Min Lin, Aldo R. Boccaccini, *Materials Chemistry and Physics* 103 (2007) 95–100
5. J.Li, B.Fartash and L.HerrnanssonS, *Biomaterials* 16 (1995) 417-422
6. Nasser Y. Mostafa, *Materials chemistry and physics* 94 (2005) 333-341
7. M. Akao, *Journal of material science* 16 (1981) 809-812
8. R. I. Martin, P. W. Brown, *Journal of material science: materials in medicine* 6 (1995) 138-143
9. Carl E Misch, *Journal of oral maxillofacial surgery* volume 57 issue 6, June 1996, Pages 700-706
10. Chidambaram Soundrapandian, Sanghamitra Bharati, Debabrata Basu, Someswar Datta, *Ceramics International* Volume 37, Issue 3, April 2011, Pages 759–769
11. Horng Yih Juang, Min Hsiung Hon, *Materials Science and Engineering C2* (1994) 77-81
12. A. Joseph Nathanaela, Jun Hee Leea, D.Mangalarajc, S.I.Honga, Y.H.Rheed, *Powder Technology* Volume 228, September 2012, Pages 410–415
13. Emilija Fidancevska, Gordana Ruseska, Joerg Bossert, Yuan-Min Lin, Aldo R. Boccaccini, *Materials Chemistry and Physics* 103 (2007) 95–100

14. X.W.li, H.Y. Yasuda, Y. Umakoshi, *J Mater Sci: Mater Med* (2006)17: 573-581
15. Shekhar Nath, Rajesh Tripathi, Bikramjit Basu, *Materials Science and Engineering: C* Volume 29, Issue 1, 1 January 2009, Pages 97–107
16. Shidong Ji, Setsuaki Murakami, Masanobu Kamaitakahara, Koji Ioku, *Materials research bulletin* Volume 44, issue 4, 2 April 2009, Pages 768-774
17. T. Kokubo, H. Kushitani. S. Sakka, T. Kitsugi and T. Yamamuro, *Journal Biomed. Mater. Res.* 24, 721-723 (1990)
18. A.J.Ruys, M.Wei, C.C.Sorrell, M.R.Dickson,A.BrandwoodS and B.K.MilthomeS, *Biomaterials* 16 (1995) 409-415
19. Anna hsarczyk, Czedawa Paluszkiewicz, Marek Gawlicki & Zofia PaszkiewiczF., *Ceramics International* 23 (1997) 297-304
20. Dagmara Malina, Kamila Biernat, Agnieszka Sobczak-Kupiec, *ABP*, Vol. 60, No 4/2013 851–855