INNSPUB

International Journal of Biosciences | IJB |
ISSN: 2220-6655 (Print), 2222-5234 (Online)
http://www.innspub.net
Vol. 14, No. 1, p. 194-206, 2019

RESEARCH PAPER OPEN ACCESS

Coating evaluation of calcium sulfate nano particles on commercially pure titanium

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Key words: Nano calcium sulfate, Dip Technique.

http://dx.doi.org/10.12692/ijb/14.1.194-206 Article published on January 11, 20199

Abstract

The study aim is evaluation the effect of dip coating of commercially pure titanium implant by calcium sulfate nanoparticles. Commercially pure titanium Grade (II) rods were machined into circular shaped discs and were coated by nano calcium sulfate through using different binder (P_2O_5, PVA, PVA+PVP) the evaluation was done by using optical microscope, X-ray diffraction analysis, Atomic Force Microscope, Scanning Electron Microscope, Energy-Dispersive X-ray investigations and Vickers microhardness measurements. The most valuable results obtained by using (PVA+PVP) as binder for Cp Ti disc coated by nano calcium sulfate. Nano calcium sulfate can successfully work as coating material for titanium implant by dip coating method which increase surface Microhardness and have uniform thickness of coating layer.

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Introduction

Titanium can be applied and replacing missing teeths due to its mechanical feature that are closer to bone tissue than other material (stainless stell, chrom cobalt), titanium implants can be improved mechanically and bioactivity by chemical and physical means. A successful osseointegration process is commonly regarded as the convenient tool for success of implant treatment, precisely in patients with impaired bone healing (Palmquist *et al.,* 2010).

Calcium sulfate work as bone grafting material for many years and have the ability to degrade rapidly between 4-6 week this feature minimize the use of calcium sulfate in defect with large size, so to solve this problem nano calcium sulfate has been emerged, which degrade almost in 12 weeks (Tovar *et al.,* 2011).

calcium sulfate for bone generation which is conversion of calcium sulfate as it dissolve in body fluid to calcium phosphate that increase adherence of osteoblast to the defect site (Kokubo 2008) and calcium sulfate has been found to cause local reduction of PH which is related to bone mineralization that lead to release of osteoinductive molecule inside bone matrix activating healing stage (Borrelli *et al.,* 2003; Evaniew *et al.,* 2013)**,** the ability of calcium sulfate to work with other bone graft material as binder which improve production in the defected site (Al Ruhaimi 2000)**.**

Titanium implant Ceramic coating is one of the most commonly reported techniques (Kim *et al.,* 1999;Lee *et al.,* 2002; Bigi *et al.,* 2005). Various coating techniques like (plasma spray, dip-coating, sputtering, electrophoretic deposition, and electrochemical deposition) can be used. Dip coating is a method of surface coating by a thin fine biocompatible ceramic film of required material on titanium implant for improving the osseointegration , the samples is dipped in a solution contain the coating materials and then evacuated by a regulated speed and by planned temperature and climatic. This method is not difficult to achieve, economic and can adapt to variations of the sample surface, as compared to other coating techniques it offer many advantageous like (the control of coating morphology, flexibility, chemistry and structure) (Aksakal and Hanyaloglu 2008; Basco *et al.,* 2012; Al-Hijazi *et al.,* 2013; Rahman and Nasir 2016).

This study was performed to investigate the best percentage of mixing that improve the surface roughness and microhardness for dip coating technique for nano crystalline calcium sulfate.

Materials and methods

Commercially pure Titanium (grade 2) was cut into small circular discs (10 mm diameter and 1 mm thickness) with a lathe machine then used as the substrate for coating, these discs were grinded by silicon carbide paper starting from 500 to 1000 grit, a rotative polisher at 250 rotations per minute (rpm) for 2 minutes for each step of grinding till uniform smooth surface was obtained.

The discs were cleaned by Ultrasonic bath of ethanol used to get rid of debris and Contamination for 15 min, followed by 10 min in distilled water bath. After that the specimens left to dry at room temperature (Shukur 2016).

Optical microscopical observation

A numbers of micrograph explain the microstructure of nano calcium sulfate using Polyvinyl alcohol (PVA) as binding agent coated the Cp Ti for four times of dipping each time one minute (Figure 1), nano calcium sulfate using (PVA+PVP polyvinylpyrrolidone) as binding agent coated Cp Ti four times of dipping each time one minute (Figure 2) for the same time under different magnification power (100µm, 250µm).

Atomic force microscope

The surface roughness analysis produced by the atomic force microscope for Cp titanium, coated by nano calcium sulfate using PVA as binding agent and another sample that use PVA and PVP as binding agents to choose the best sample, Scanning probe microscope investigations shows projections and peaks with the average grain size , average roughness and the sample granulation distribution charts.

Film thickness

The thickness of the coated layers was measured by the Erichsen mini test micro process thickness gauge. The coating thickness of the coated film was increased with the increasing of the coating time.

Solution preparation

The coating solution of nano calcium sulfate was done by:

The addition of nano calcium sulfate (10 g) to 50 ml NaCl in glass container and heating at 45 ºC on hot plate stirrer for half an hour, to get a homogenous solution (according to manufacture instruction).

Addition of (0.01g) of P_2O_5 to the previous solution. A second solution was prepared by addition of PVA (0.5g) to solution of nano calcium sulfate (10g) in the 50 ml of NaCl. The temperature was maintained at approximately 45 ºC, the mixture left over a stirrer for half an hour to gain homogenous solution.

The third solution was prepared by the same procedure of the second solution except the addition of (0.5g) of PVP to the PVA (0.5g).

The coating was done by using a device locally manufactured for dip coating that hold the discs by braces and contain time regulator to control the immersing time of the discs in the mixture solution for (30 sec, 60sec) and withdrawn with a well defined with drawl speed, dried for one minute at room temperature and then returned to its coating solution. Disc coating was made by immersing the discs in nano calcium sulfate solution for (60) sec four times. After dipping procedure, each coated sample was left for 24 hour at room temperature for drying.

The solution that used P_2O_5 as a binder, the coating layer was detached easily and not bind with Cp Ti substrate so it's cancelled from this study.

Heat treatment

Heat treatment of the nano-calcium sulfate was carried out for densification using carbolated furnace (tube furnance) under the presence of inert gas (argon) to avoid oxidation of titanium disc, the sintering of nano-calcium sulfate coated disc was tried at different temperature (200, 400, 550, 600 ºC), for 2hour, the most appropriate heat treatment was (550 ºC) for 1 hour (Harel *et al.,* 2006).

X-ray Diffraction analysis

The XRD pattern for titanium coated with calcium sulfate nano powder with presence of PVA in (figure 7) shows an identical match with International Centre for Diffraction Data (ICDD 37-1496) for calcium sulfate in peaks (111) , (020), (121), (040) and (224) and identical match with (ICDD 44-1294) for titanium in peaks (002), (101) and (102).

The PVA doesn't appear because it is evaporated after heat treatment, while for titanium coated with calcium sulfate nano powder with presence of PVA and PVP (figure 8) shows an identical match with (ICDD 37-1496) for calcium sulfate in peaks (111), (020), (121), (040) and (224), and identical match with (ICDD 44-1294) for titanium in peaks (100), (002), (101) and (102).

The PVA and PVP didn't appear because they are evaporated after heat treatment.

Microhardness test

An average of four readings from four groups of Cp Ti samples, the first group contain uncoated samples or specimens, the second group contain specimen that coated by 2 layer each one (60 sec), the third group specimen that coated by 3 layer of each one (60sec) and the fourth group contain specimen coated with 4^{th} layer each one of (60 sec).

The Vickers microhardness tester were taken to describe the indentation hardness, Vickers hardness was installed to use (1) Kg load and (5) sec loading time, the average hardness Vickers (HV) numbers are seen in table below.

Energy Dispersive X-ray spectroscopy analysis (EDX)

Energy Dispersive X-ray spectroscopy (EDX) analysis, for the main components of Cp titanium discs (uncoated, nano calcium sulfate disc by using of dip coating technique) including weight and atomic percentages of the main elements,. Usually the EDX range shows peaks matching to energy levels of which X-ray collects.

Every one of these peaks is related precisely to an atom, so it match to a single component, as the peaks are higher in the spectrum, the increased percentage of the component in the sample (Kumar *et al.,* 2013).

EDX analysis showed the presence of Oxygen, Carbon and Calcium as the major component in coated Disc. SEM\EDX mapping showed Titanium even distribution in dip coated disc.

Results

Figures 3, 4, 5, indicate the granulation distribution charts of the dip coated nano calcium sulfate using PVA and PVP while Figure 6 shows the relation of nano calcium sulfate coating thickness layer with deposition time.

Optical microscopical observation

As depicted in figures 1 which indicates A numbers of micrograph explain the microstructure of nano calcium sulfate using Polyvinyl alcohol (PVA) as binding agent, while figure 2 indicates the nano calcium sulfate using (PVA+PVP polyvinylpyrrolidone) as binding agent for the same time under different magnification power (100μm, 250μm).

Atomic force microscope

This measurements data as below:

Table 1.

Sample surface	Average roughness	Average grain size
Machine cut (control)	0.026 nm	74.65 nm
Dip coated nano calcium sulfate with PVA	2.53 nm	84.33 nm
Dip coated nano calcium sulfate with PVA+PVP	3.28 nm	91.66 nm

Microhardness test

An average of four readings from four groups of Cp Ti samples measurements is shown in table below:

Scanning electron microscope (SEM) analysis

Morphological analysis, by using scanning electron microscope for Cp Ti discs (uncoated and coated with nano calcium sulfate by using of dip coating techniques) as shown in (figure 9,10) the changes in the surface appear at different magnification in the coated disc there are various polycrystalline structure of nano calcium sulfate agglomerate over each other forming a bigger structure.

Table 2.

Group name	Average hardness
Uncoated sample	230.4
Two layer coated sample	237.6
Three layer coated sample	248.6
Four layer coated sample	254.3

Energy Dispersive X-ray spectroscopy analysis (EDX)

Energy Dispersive X-ray spectroscopy (EDX) analysis, are showen in(figure 11,12), while EDX analysis showed the presence of Oxygen, Carbon and Calcium as the major component in coated Disc. SEM\EDX mapping showed Titanium even distribution in dip coated disc (figure 13).

Discussion

In this study PVP also used as binding agent for multiple reasons which are: pH-stable, non-ionic, non-toxic, strong coordination ability and excellent biocompatibility, PVP during sintering procedure evaporate without leaving a remnants on the surface, PVP is applied as coatings for medical uses because, it forms pores on plastics and hydrophilizes, minimize the toxicity of the precise elements, stabilizes the enzymes and vitamins and it minimize cell adhesion, protein adsorption, encrustation biofilm and formation. Also PVP able to produce a thin film with crack free like (TiO_2, $BaTiO_3$) (Yoshida and Prasad 1996; Kozuka and Kajimura 2000; Zheng *et al.,* 2000; Deng *et al.,* 2008; Folttmann Quadir 2008).

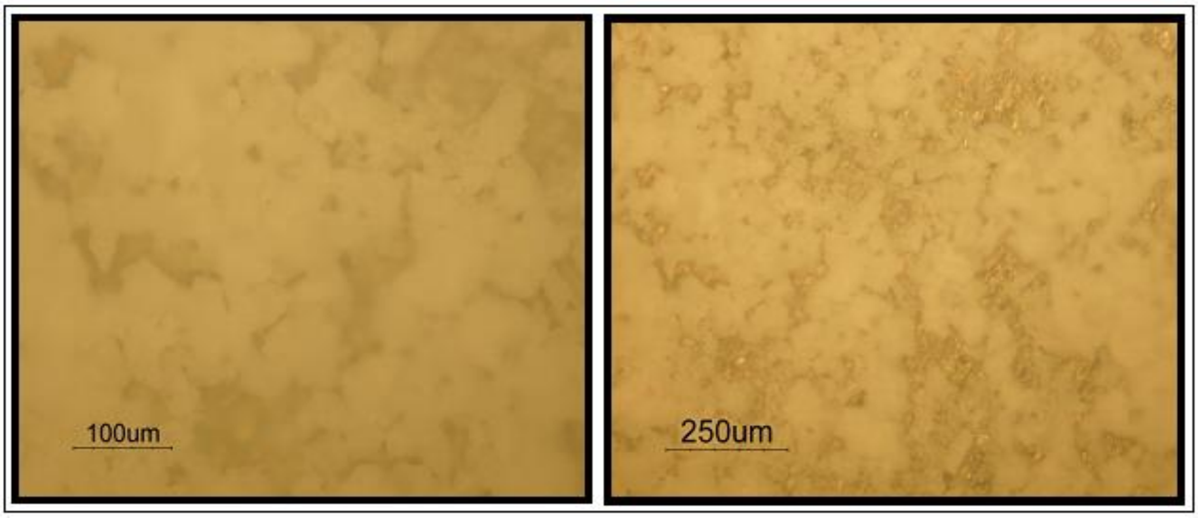


Fig. 1. Nano calcium sulfate coating with PVA (1000x, 2500x).

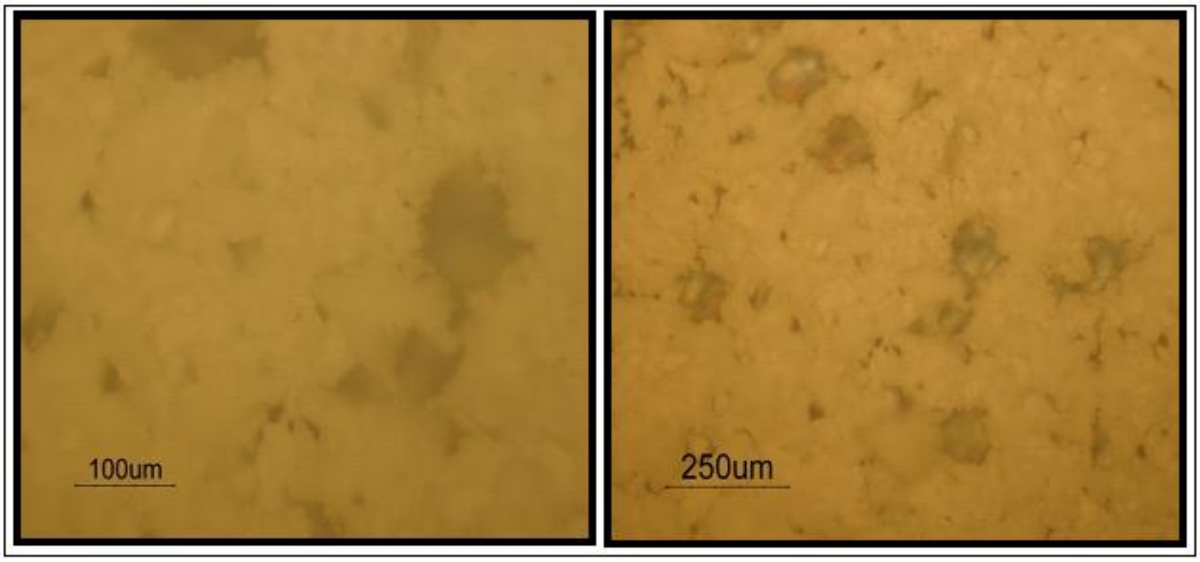


Fig. 2. Nano calcium coating with (PVA+PVP) (1000x, 2500x).

From the result of optical microscope showed that nano calcium sulfate uniformly distributed and dense on the titanium disc with holes on coating film, while the dip coated nano calcium sulfate using PVA and PVP showed that nano calcium sulfate uniformly distributed and dense on the titanium disc with less number of multiple holes on coating film.

Morphological analysis, by using SEM for Cp Ti disc coated with nano calcium sulfate with (PVA+PVP) as a binding agent has confirmed the optical microscopical result for dip coated disc, beside, it clarify the blending of small poly crystalline structure over each other forming a bigger poly crystalline structure size (figure 10).No cracks appears on SEM analysis in the coated disc due to no shrinkage environments in the coated layer of nano calcium sulfate, also from the use of PVP, holes appear as a result liquid phase evaporation which related to the solution type and coating film thickness (Santillán *et al.,* 2010).

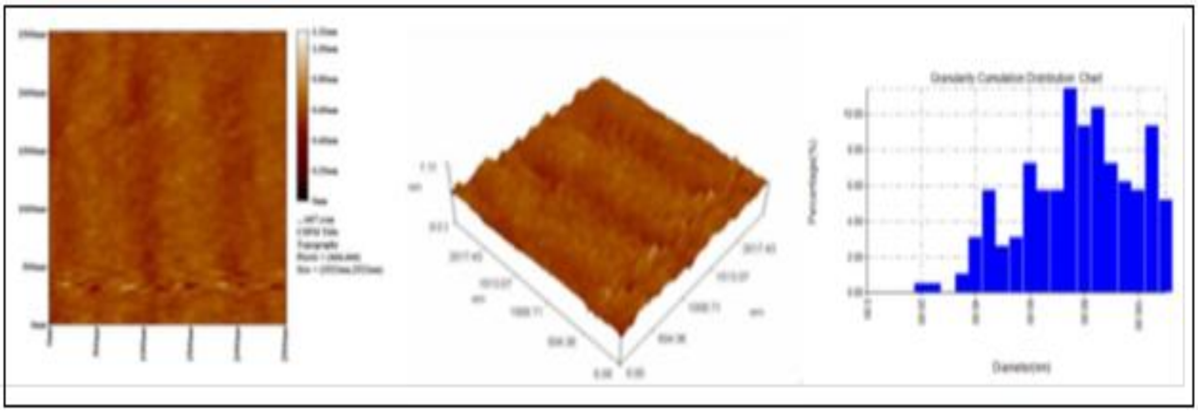


Fig. 3. AFM topographies and granulation distribution charts of machine cut CPTi.

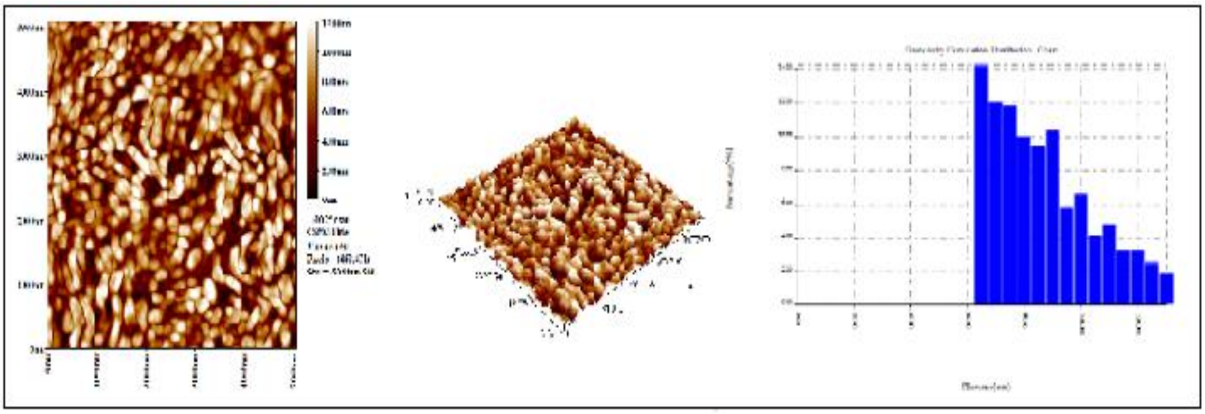


Fig. 4. AFM topographies and granulation distribution charts of the dip coated nano calcium sulfate using PVA.

The holes also may appeared due to incomplete spread of particle (Su *et al.,* 2018). From Atomic force microscopy ,In this study, both PVA and (PVA+PVP) were used as binder for coating of nano calcium sulfate, the coated discs showed coating film that have nano-rough surface, that was appeared also in morphological analysis (Figure 10).

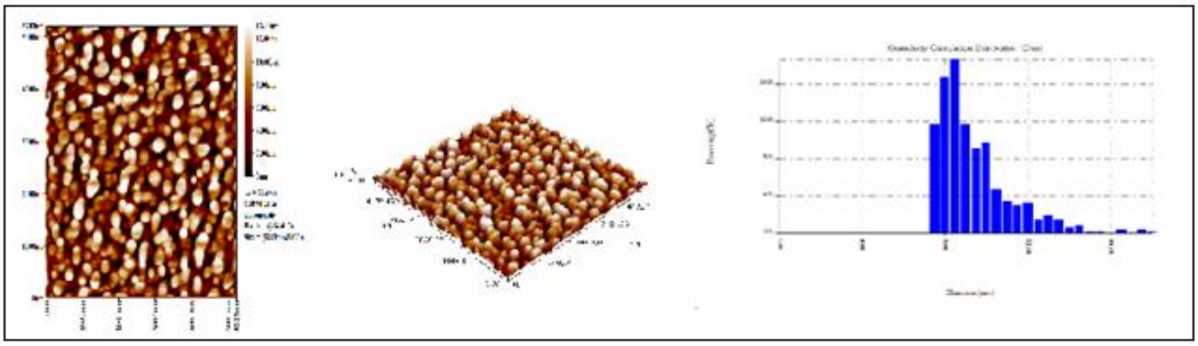


Fig. 5. AFM topographies and granulation distribution charts of the dip coated nano calcium sulfate using PVA and PVP.

Dip coating technique was used as it improve purity and strength of the coating layer on Cp Ti substrate (Choi *et al.,* 1999; Hsieh *et al.,* 2001; Liu *et al.,* 2002; Milev *et al.,* 2003). Calcium sulfate set more quickly with blood, so calcium sulfate that is preset should be applied as bone graft material it dissolve more consistently and slowly than calcium sulfate that use blood for setting.

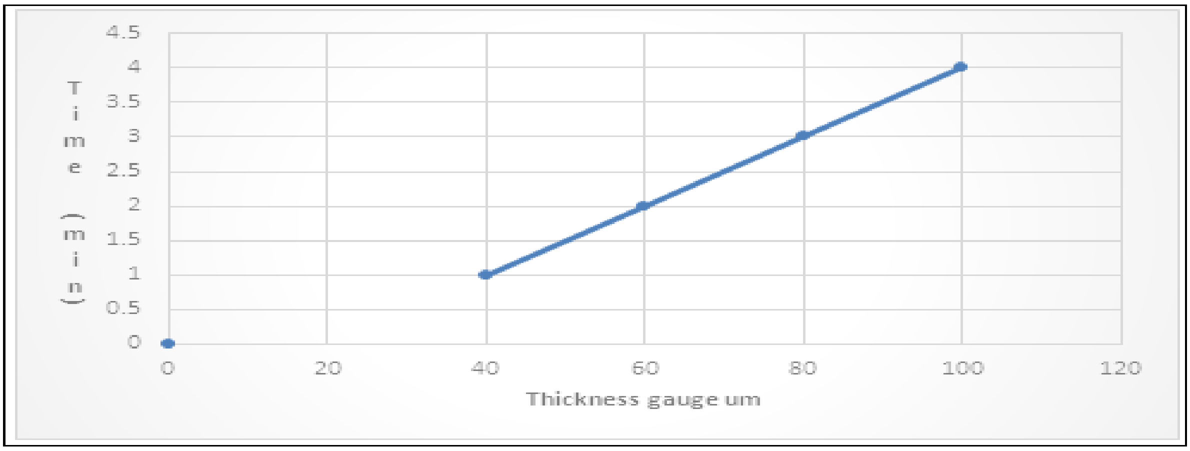


Fig. 6. The relation of nano calcium sulfate coating thickness layer with deposition time.

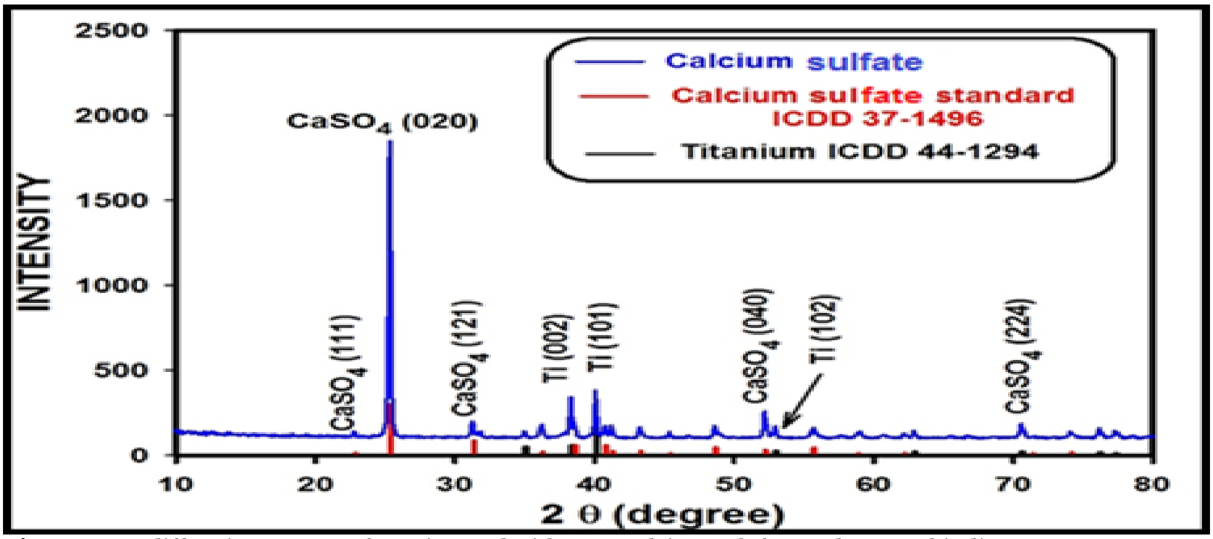


Fig. 7. X-ray diffraction pattern of Cp Ti coated with nano calcium sulafate and PVA as binding agent.

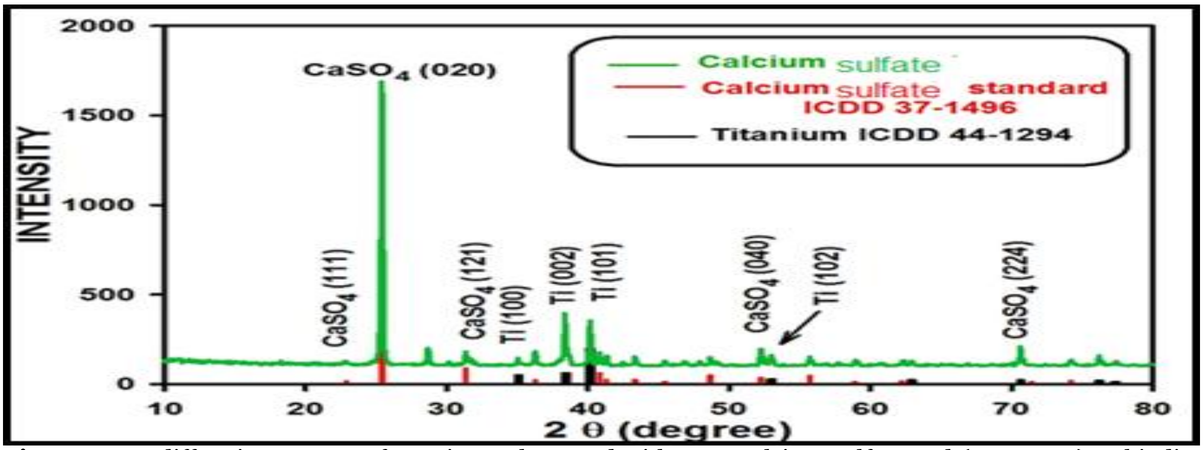


Fig. 8. X-ray diffraction pattern of Cp Ti sample coated with nano calcium sulfate and (PVA, PVP) as binding agent.

In bone region usually it's preferable to work in dry condition to reach good setting. A good setting in calcium sulfate is achieved using NaCl which accelerate the setting of calcium sulfate (Pecora *et al.,* 1998; De Leonardis and Pecora 1999). The PVA was chosen as binding agent to improve adhesion strength due to its polar nature which increase strong adhesion between PVA and other molecule (Mollazadeh *et al.,* 2007; Sinha and Guha 2009), as well as the PVA has accepted biocompatibility which is another reason to choose PVA as binding agent (Kobayashi *et al.,* 2004; Rusu *et al.,* 2005).

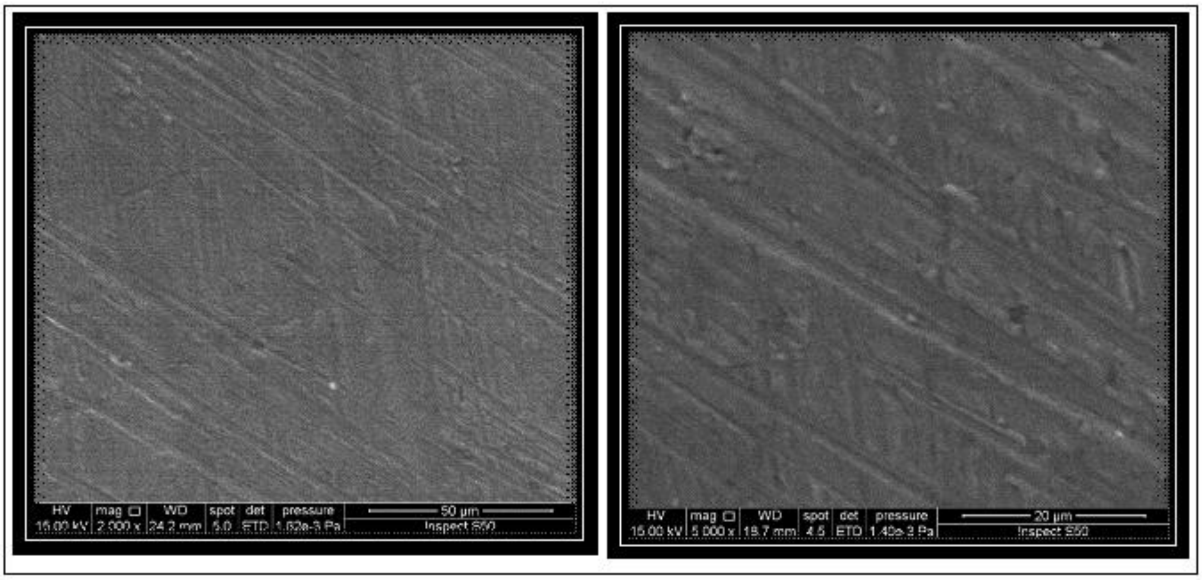


Fig. 9. SEM of uncoated Cp Ti disc with different magnifications power (50, 20 µm).

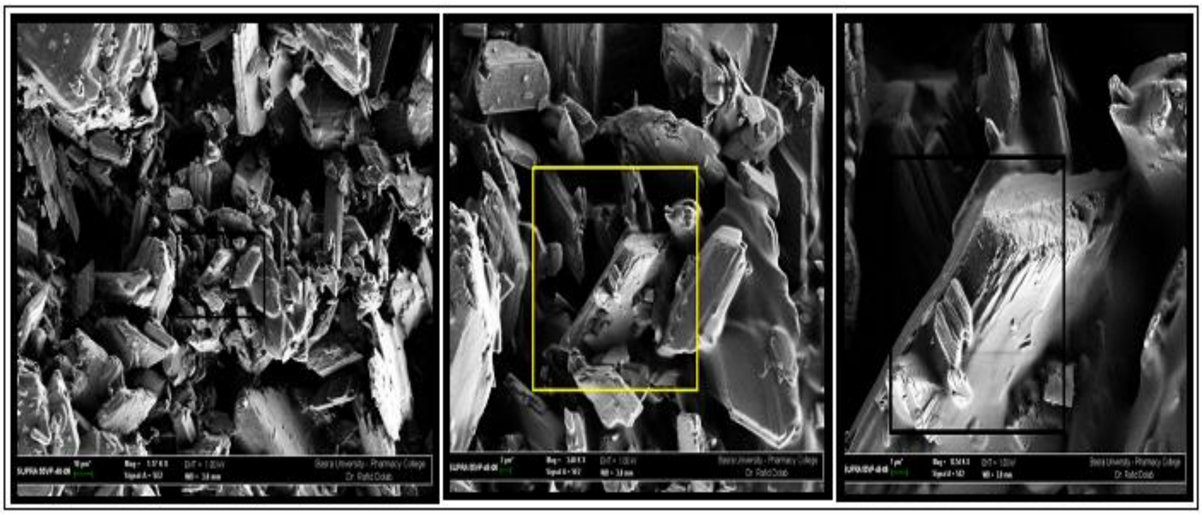
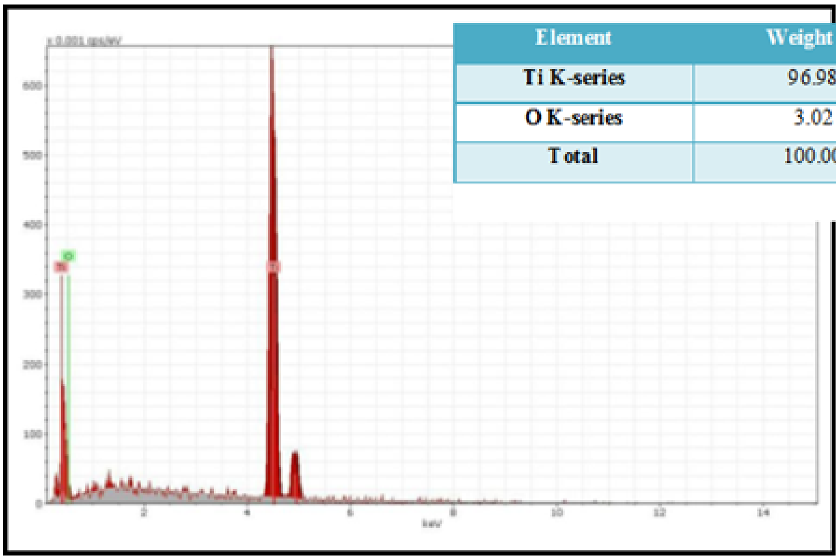


Fig. 10. SEM of coated Cp Ti samples by dip coating techniques with several magnifications.

The nano calcium sulfate solution appear to have the most effective result when used with (PVA+ PVP) as binding agent when compared to nano calcium sulfate solution that use only PVA as binding agent, The two coated disc has approximately the same granulation distribution with more uniform distribution of grains in (PVA+PVP) and surface roughness for (PVA+PVP) as binding agent was (3.28 nm) while for PVA alone was (2.53 nm), so (PVA+PVP) was chosen so that the surface area was increased with increased in surface roughness on implant surface that promote bone apposition (Albrektsson and Wennerberg 2004).

It is obvious from of the XRD schemes (figure 7, 8), that the surface of the disc was well coated with nano calcium sulfate using PVA alone and (PVA, PVP) as binding agent respectively, because most of the diffraction peaks could be indexed to calcium sulfate matching to with (ICDD 37-1496) for calcium sulfate in peaks (111), (020), (121), (040) and (224). The presence of Titanium peaks in the XRD pattern after each coating process was due to the penetration of X-rays beyond the coated layer.

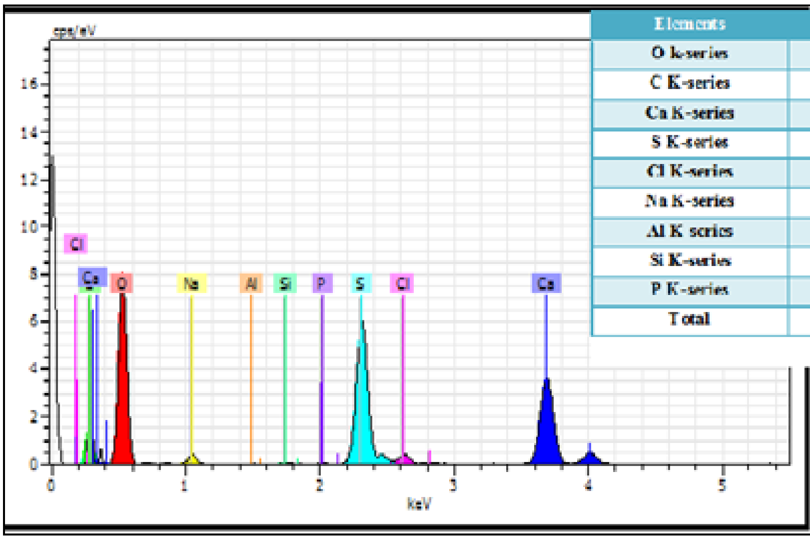


Element	Weight %	Atomic %
Ti K-series	96.98	91.47
O K-series	3.02	8.53
Total	100.00	100

Fig. 11. EDX analysis for uncoated disc.

The narrower peaks of XRD are related highly crystalline nature of layers, while broad peaks showed decreased levels of crystallinity, this explaination in agreement with Ladd 2013 (Ladd 20.13).

Vickers microhardness test for the uncoated and coated nano calcium sulfate discs indicates that the average Vickers hardness (HV) numbers are (230.4uncoated group), (237.6 two coated layer), (248.6 three coated layer), (254.3 four coated layer) These changes in Vickers numbers are appeared because of the variation of surface topography between the coated and uncoated titanium discs, while for coated nano calcium sulfate groups as the number of coating layer increase will lead to increasment in film thickness, consequently Vickers hardness number increased.



Elements	Weight%	Atomic%
O k-series	53.78	60.38
C K-series	16.31	24.39
Ca K-series	15.84	7.10
S K-series	11.89	5.65
Cl K-series	1.07	0.04
Na K-series	0.80	0.65
Al K series	0.03	0.02
Si K-series	0.08	0.05
P K-series	0.04	0.02
Total	100.00	100.00

Fig. 12. EDX analysis for nano calcium sulfate coated disc.

EDX analysis in (figure 11, 12) of the uncoated disc and the coated nano calcium sulfate groups showed that the mutual component in the surface of the all discs was O. the coated nano calcium sulfate showed increased surface oxide percentage as compared to uncoated one due to oxygen content in calcium sulfate hemihydrates (Sandeep 2014), or because of incensement in titanium dioxide film thickness (Hamouda *et al.,* 2014), who stated in (EDX) plot the increase in oxygen percentage is connected to increasment in Titanium dioxide that formed on Cp Ti disc, also increase of oxygen in titanium percentage may be related to oxidation as consequence of high temperature of sintering (Kumar 2013), the appearance of carbon in (EDX) analysis of coated titanium disc, because carbon considered as dielectric fluid with remnants usually contain carbon (Kumar 2013).

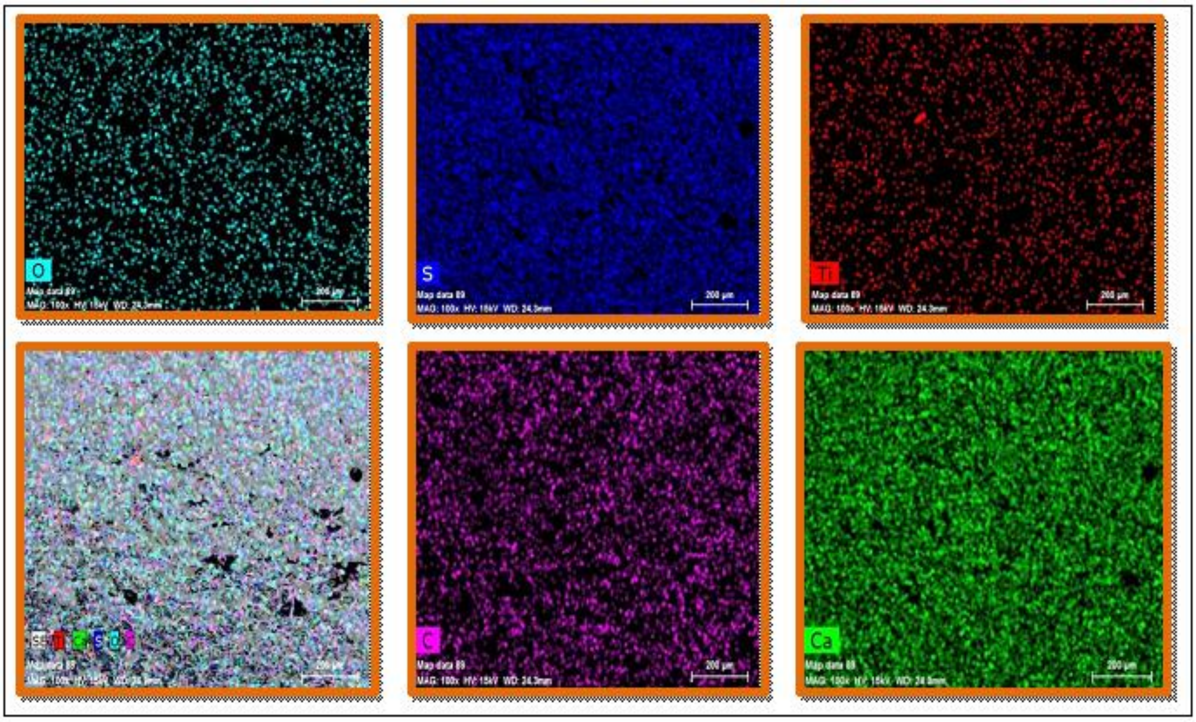


Fig. 13. EDX mapping for nano calcium sulfate coated disc.

In (EDX) mapping confirm the uniform distribution of particle. And the main element of coated disc are (O, S, Ca) (Zwain and Hamad 2018).

Conclusion

Nano calcium sulfate can successfully work as coating material for titanium implant by dip coating method which increase surface Microhardness and have uniform thickness of coating layer.

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