Investigating Commercial pure titanium corrosion behavior and a few other characteristics after being coated with a chitosan-hydroxyapatite nanoparticle mixture in a lab experiment

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Abstract

Introduction: Metals like titanium and its alloys are frequently used in the construction of medical equipment like dental and orthopedic implants. However, the presence of blood and other bodily fluids in the immediate surroundings may cause corrosion to this implant.

Materials and Methods: The preparation of circular discs of commercially pure titanium (Cp-Ti) measuring 10mm in diameter and 2.5mm in thickness. To precipitate the coating layer, Ti samples have been immersed in a solution of Hydroxyapatite (HA) and chitosan for 90 minutes on a low-speed stirrer. Samples were taken out and dried in the air as the initial coating step, and then they were immersed in the mixture once more for 15 minutes before being taken out and dried in a hot air oven (200 °C).

Results: The results of coated titanium samples have demonstrated diverse surface features, with the present roughness connected with the appearance of a crystal pool and irregular accumulations of small, spherical-like grains. Thickness measurement found that the average thickness readings were 60 um. The Energy dispersive x – ray studies revealed the presence of ions that made up the HA. The open circuit potential (OCP) corrosion test and ANOVA test revealed that coating with hydroxyapatite and chitosan significantly reduces the corrosion rate.

Conclusions: Coating titanium implants with HA or chitosan will, respectively, speed up and slow down the pace of osseointegration and corrosion.

Keywords: Commercial pure titanium (CP – Ti), Dip coating, Chitosan, Dental implant, Corrosion

Introduction:

The titanium and its alloy can be considered as "gold standard" material for endosseous dental implants between all the available dental implant materials, their position distinguished due to its many desirable properties beside their long-term clinical survival rates for several decades. The titanium and its alloys able to interact closely with the tissue bone beside its highly biocompatible (spontaneous build-up of an inert and stable oxide surface layer (1). The usage of Titanium (Ti) and its alloys as dental implants may be correlated with some disadvantages despite the well evidenced of its usage like, the elastic moduli difference between the titanium implant and the surrounding bone, which led to stress in the bone-implant interface and periimplant bone loss (2), its dark grayish color (3) and hypersensitivity to titanium (4). Those limitation of the titanium and its alloy coupled with the patients demanding for dental implants metal-free led to using the dental implants made from ceramic and polymer (5); but unfortunately, due to high young`s modulus of the ceramic led to preferring using of polymer (6). The surface of titanium biomaterials for bone implants is usually subjected to modifications aimed at improving osteointegration properties, providing resistance to corrosion, or delivering a therapeutic substance to the perivascular tissues. For this purpose, the surface layer of the implant is modified or a specific coating is deposited (7,8,9,10).

Great adherence to metallic surfaces under shear loads, appropriate roughness, and high resistance to corrosion phenomena should all be present in coatings for implants (11). However, despite being subjected to severe loads during the implantation operation, such structures frequently display a weak adherence to the metallic substrate (12). Higher wettability and the capacity to absorb proteins from surrounding body fluids are two characteristics of the resulting nanotubes of nanometric diameters (13). Additionally, these features can lessen bacteria's ability to stick to implant surfaces. The resulting layer sticks firmly to the substrate, resists scratching, and is unaffected when the substrate is bent (14). The osteointegration characteristics of the nanotubes can be further enhanced by adding different proteins to their surface. Additionally, it is feasible to put a therapeutic chemical inside of them, creating a powerful drug delivery system (15). Investigative work is still being done on the creation of a surface treatment based on the removal of material using physical, chemical, and electrochemical processes. In order to prepare implant surfaces for coating deposition, there are a number of more sophisticated techniques available, including micro-arc oxidation (MAO) (16), ion implantation (17), laser modification (18), and friction stir processing (19). However, these techniques are more expensive and call for more complicated equipment (20). After achieving a specified level of roughness and morphology, the challenge moving forward is to make titanium surfaces that mimic biological surfaces. The paradigm for implant surface technology is altering, therefore scientists are turning to nature for direction. Human bone already contains hydroxyapatite (HA) (21). These nanometer-sized calcium phosphate crystals, which can be up to 5–20 nm wide and 60 nm long, make up a considerable amount of the mineral content of bone. A particular hemostatic level of HA is always maintained in live bone via a cycle of osteoclastic and osteoblastic activity (22). HA has been rigorously used in research and clinical settings in a variety of shapes and forms because it is a bioactive and biocompatible substance (23). HA might affect how proteins interact, resulting in improved healing and increased osteoblast adhesion, proliferation, and differentiation (24,25).

The multiple methods of applying HA coating to various surfaces are covered in great detail in the literature. There have been reports of wet chemical deposition, thermal plasma spraying, pulse laser deposition, sol-gel, electrodeposition, and biomimetic deposition among these techniques (26). The biomimetic deposition approach, in which a simulated bodily fluid (SBF) solution is created in line with the inorganic components of the human blood plasma, is one of the simplest ways among those that meets the varied needs of implant therapy (27,28). Numerous publications attest to the fact that SBF produces apatite crystals that resemble human bone on surfaces like titanium (29,30,31). The ability of an implant material to attach to nearby living bone is frequently determined by the capacity to create this apatite layer (32). This bioactive buildup can promote the formation of new bones and the healing process. Consequently, it is possible to confirm early osseointegration of titanium implants (33 – 38). A variety of medicinal or biomimetic substances can be included in the layer that forms on titanium surfaces when SBF is used to coat them. This provides new opportunities for improving the implant surface medicinally or bio-mimetically to ensure a steady discharge of the surface components (39,40)

Aim of this study to evaluate the effect of nano hydroxyapatite, chitosan and collagen composite coating, nano hydroxyapatite and chitosan composite coating with nano hydroxyapatite coating on commercially pure titanium implants by dip coating. The Null hypothesis stated that there was no effect of chitosan/ HA mixture coating on the corrosion behavior and other properties. While the Positive Alternative Hypothesis stated that the mixture of Chitosan/ HA coating will enhance the ability of CPTi to resist corrosion. And the Negative Alternative Hypothesis stated that the mixture of Chitosan/ HA coating will reduce the ability of CPTi to resist corrosion.

Materials and Methods:

Sample preparation:

Commercially pure titanium (Cp-Ti) discs with a diameter of 10 mm and a thickness of 2.5 mm have been created as follows: Silicon carbide with a 500-micron roughness was used to cut and mirror polish Cp-Ti rod grade 2 (Orotig Srl., Italy) for 15 minutes. The discs were then cleaned in an ultrasonic bath with 99.8% ethanol to remove contaminants and debris. The discs were cleaned for 15 minutes; they were then dried at room temperature after being washed with distilled water for 10 minutes (41).

Dip coating procedure:
Using a magnetic stirrer, 3 grams of HA powder were combined with 25 milliliters of distilled water, and the mixture was continued until all of the ingredients had been dissolved. The slurry was separated into three groups (A, B, and C), and then chitosan was added to the slurry on a magnetic stirrer at concentrations of: (0.5 gm for group A, 1 gm for group B and 1.5 gm for group C).
To precipitate a coating layer, titanium samples were immersed in a solution of HA and chitosan on a stirrer for 90 minutes at a low speed. The samples were then taken out and dried in the air as the first layer of coating, immersed in the mixture once more for 15 minutes, and dried in a hot air oven (200 ^{o}C) (IMS/406, France). (42)

Heat treatment:
A tube furnace (Carbolite Type MTF12/38-A. BAMFORD, U.K.) was used for the sintering, which took place at 4000C for a whole hour (43).

Analysis of coating layer:
The specimens' coated surfaces underwent the following analysis:

Thickness measurement:
A micro-process coating thickness gauge was used to measure the thickness of the coating layer (TF-C-UVIS-SR, USA). The average of the three readings was 60 mm after three readings were taken and their average was calculated. As seen in figure 1.

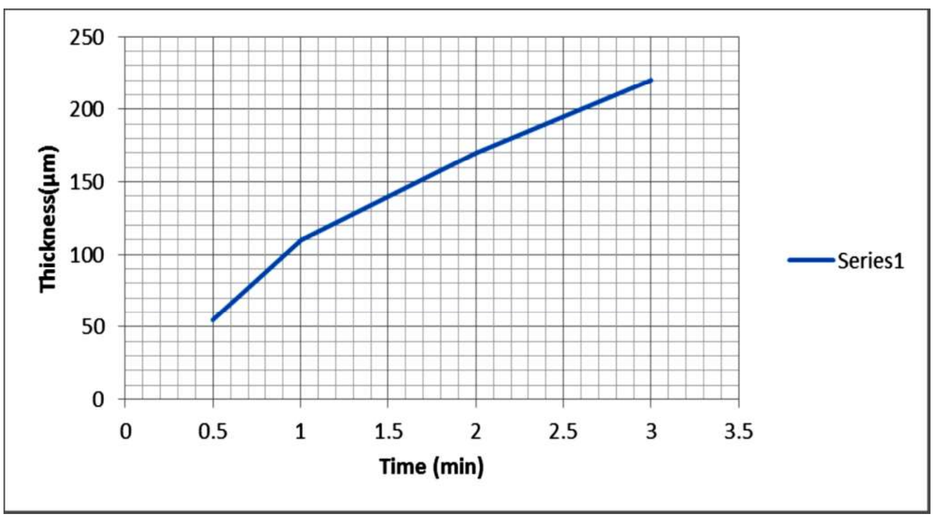


Figure 1: Chitosan and nano-HA coating thickness at 0.5, 1, 2, and 3 minutes

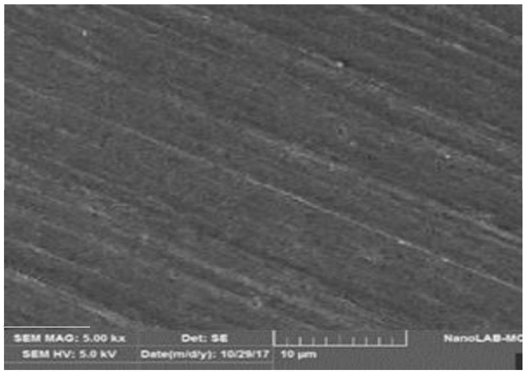
Structural surface characterization by SEM:
- Surface analyses: Using a scanning electron microscope, the topographical characteristics and surface morphology of the coated sample were determined (TESCAN Vega 111, Czech Republic).
- Energy Dispersive X-ray (EDX): To assess the makeup of the coated layer (44)

Electrochemical Corrosion:
Since it requires a channel for the transfer of electrons and water, this type of corrosion is also known as "wet corrosion." Five Titanium samples were examined using the apparatus, including uncoated, HA-only, and coated with chitosan/HA ratios of 0.5, 1, and 1.5%/wt. (Parstat 2273, USA). This was made up of electrolytes that mimicked bodily fluids and two electrodes (a cathode and an anode) (45).

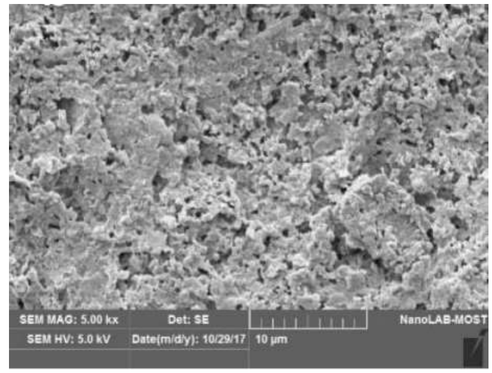
Results

Scanning electron microscope (SEM):

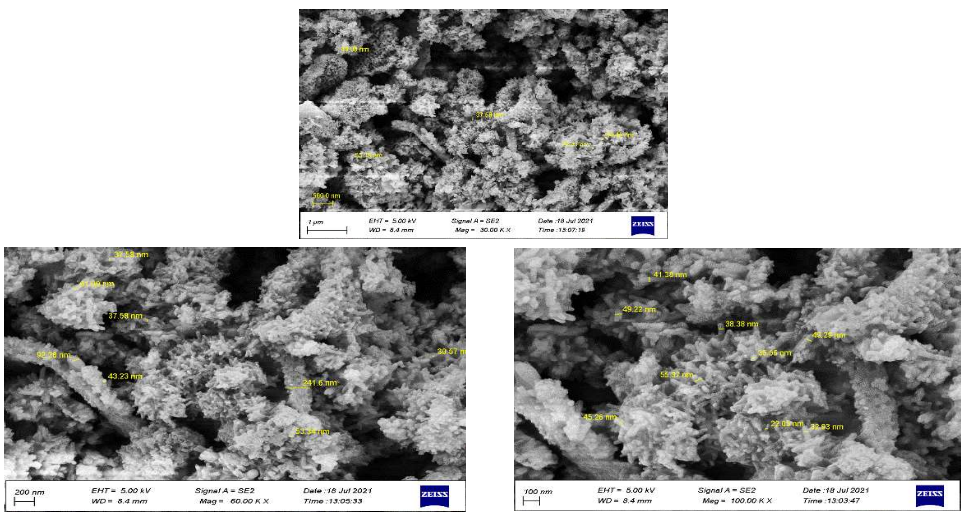
The uncoated titanium sample showed a smooth surface, but SEM of the coated film revealed varied surface features, including rough surfaces with uniform and crack-free distribution of the particles and the appearance of a crystal pool with aggregation of tiny, spherical-like granules. One of HA's characteristics is this mode of buildup. As seen in figure 2 (A ,B and C)



A. SEM of uncoated



B. SEM of coated titanium with HA only



C. SEM of titanium sample coated with HA and chitosan

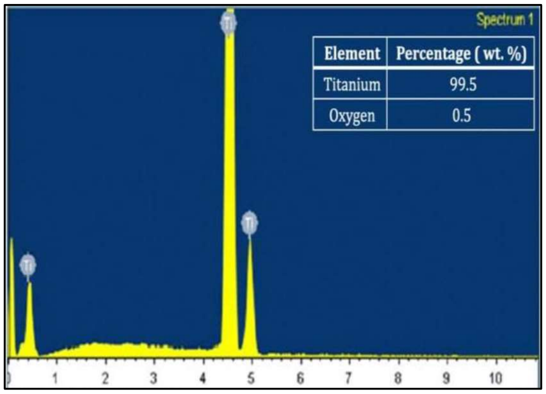
Figure 2: SEM of titanium (A, B and C)

Energy Dispersive X-ray (EDX):

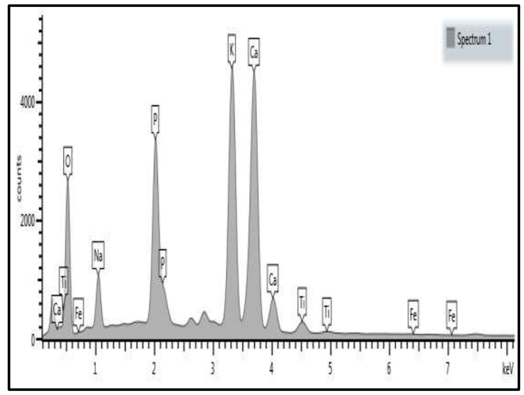
Figure 3 shows the results of an EDX analysis performed on titanium samples that were untreated, coated with HA, or coated with HA plus Chitosan. According to the EDX data, phosphorous ions were incorporated into titanium at a higher concentration than Calcium ions or potassium ions. This proves that the Chitosan and Hydroxyapatite coating on titanium was applied properly. According to EDX mapping, there are also C and O_2 ions present in addition to calcium and phosphorus ions.

Corrosion test:

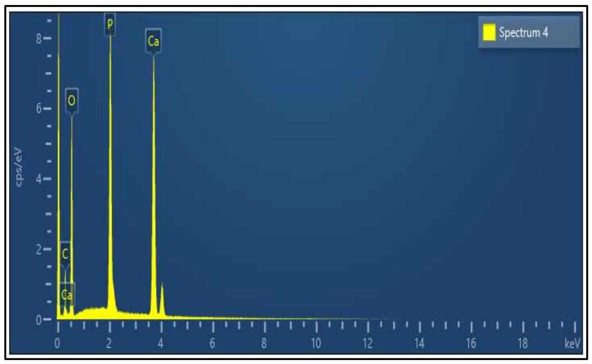
According to descriptive data, the likelihood of titanium corroding has decreased, and the corrosion resistance of the Hydroxyapatite coating has increased as chitosan has been applied. In comparison to the control group, 1.5% of chitosan and hydroxyapatite showed the highest corrosion resistance. As shown in Table 1.



A. EDX of pure titanium



B. EDS of titanium coated with HA



C. EDX of titanium sample coated with HA and Chitosan

Figure 3: EDX of coated and uncoated samples

Table 1: Descriptive statistics for Corrosion Rate value

	N	Mean	Standard Deviation	95% Confidence Interval for Mean		Min	Max
				Lower Bound	Upper Bound		
Control	5	0.0177	0.0005	0.0170	0.0184	0.017	0.018
Group 1 (HA)	5	0.009	0.00004	0.0097	0.0098	0.009	0.01
Group 2 (HA+ 0.5% Chitosan)	5	0.005	0.0002	0.0045	0.0051	0.005	0.005
Group 3 (HA+ 1% Chitosan)	5	0.003	0.0001	0.0022	0.0027	0.002	0.003
Group 4 (HA+ 1.5% Chitosan)	5	0.002	0.0003	0.0009	0.0018	0.001	0.002

The Bonferroni test also showed a very significant increase in corrosion resistance between all groups compared to the control group, as did the ANOVA test, when comparing all coating groups to pure titanium. according to table 2.

An extremely large improvement in corrosion resistance was observed between each experimental group and the experimental coating group. Observed in table 3.

Table 2: ANOVA Table comparison for corrosion rate

	Summation of the Squares	df	Mean Square	F	Sig.
Between Groups	0.0009	4	0.0003	2152.990	HS
Within Groups	0.0000	20	0.0000		
Total	0.0009	24			

Table3: Multiple comparison Bonferroni test for corrosion rate among all groups

(I) Groups		Mean Difference (I-J)	Sig.
Control	Group1 (HA)	0.0078	HS
	Group 2 (HA+ 0.5% Chitosan)	0.0128	HS
	Group 3 (HA+ 1% Chitosan)	0.0152	HS
	Group 4 (HA+ 1.5% Chitosan)	0.0163	HS
Group 1 (HA)	Group 2 (HA+ 0.5% Chitosan)	0.0049	HS
	Group 3 (HA+ 1% Chitosan)	0.0073	HS
	Group 4 (HA+ 1.5% Chitosan)	0.0084	HS
Group 2 (HA+ 0.5% Chitosan)	Group 3 (HA+ 1% Chitosan)	0.0023	HS
	Group 4 (HA+ 1.5% Chitosan)	0.0034	HS
Group 3 (HA+ 1% Chitosan)	Group 4 (HA+ 1.5% Chitosan)	0.0010	HS

Discussion:

Galvanic corrosion is the most prevalent type of corrosion and is typically found in dental implants. The material of choice for end-osseous implantation has been determined to be titanium. Titanium does not corrode when utilized in living tissue, according to long-term studies and clinical observations, but corrosion may occur when titanium is galvanically coupled to other metallic restorative materials. As a result, the choice of material for the superstructures covering the implant is quite important. Gold alloys are frequently used as superstructures due to their superior biocompatibility, corrosion resistance to corrosion, and mechanical properties. The price of valuable alloys used in dentistry is increasing, which has caused the development of more cheap metallic materials (46,47) The biocompatibility and corrosion resistance of these new diverse alloys, including Ag-Pd, Co-Cr, and Ti alloys, are of concern. Despite their high mechanical qualities and cost-effectiveness. When different alloys come into direct touch with one another inside the tissues or in the mouth cavity, galvanic corrosion results. Galvanic coupling and pitting corrosion are two related phenomena that are related to how complicated the electrochemical process is at the implant-superstructure joint (48). According to ASTM, galvanic corrosion is the expedited deterioration of a metal due to electrical contact with a more noble or nonmetallic conductor in a corrosive environment. When two or more dental prosthetics made of various alloys come in contact and are exposed to oral secretions, an electric current may be able to pass between them (49).

The development of an in vivo galvanic cell causes the galvanic current to accelerate the corrosion of the less noble metal. Through the metal-metal interface, galvanic current enters the tissues, causing discomfort. Saliva or other oral liquids, as well as bone and tissue fluids, are two electrolytes through which the current passes. It has been shown that the degree of roughness on the surface of a dental implant has a substantial impact on the bone that surrounds it (50). It is a significant factor that might have an impact on how osteoblasts adhere to titanium surfaces. Studies reveal that average Sa values between 1 and 2 µm are ideal for osseointegration at the bone-implant contact (51, 52). Sandblasting and acid etching was therefore done on the surfaces to increase the surface area for bone contact and thereby promote efficient implant treatment (53). It was possible to obtain a surface that was comparable to the acid-etched surface of commercial implants with a surface roughness of between 1 and 2 µm. The sandblasting procedure, which typically embeds alumina particles in the sample, left behind surface contaminants that might be removed by the acid etching procedure (54). Alumina was not detected in any sample during the EDS and XRD investigation of the surfaces. Recent research recommends applying various biomimetic coatings after surface modification to improve the efficacy of implant therapy (55,56). Due to its well-established osteoconductive qualities, a HA surface coating was used in this study on the samples (57). It was done utilizing a biomimetic method that makes use of the positive effects of coating titanium surfaces with HA using Tas-SBF solution. The SBF can help a HA layer on titanium surfaces achieve crystallinity and shape resembling that of apatite that resembles bone (58). This study supports the idea that coatings with more crystallinity appear to delay HA resorption, which is a positive finding (59). After the experiment was complete, the surface roughness of the SBF-coated samples in this study significantly increased. This is significant to note because, as a result, the layer may increase the area available for cell adhesion and growth. Peaks for the -OH bond were visible in the FTIR spectrum analysis, indicating the presence of HA on the surface. Peaks in the XRD results indicated that crystalline HA phases were also present. The findings indicate that it was feasible to apply bioactive thin and essentially uniform coatings of HA in this investigation to surfaces made of both pure titanium and titanium alloy. Another crucial factor is the length of immersion in the Tas-SBF solution, which affects the HA/calcium phosphate coating's surface roughness and crystal size. Typically, biomimetic coating procedures last between seven and fourteen days (60). However, various treatment techniques can significantly shorten the SBF immersion period and alter the composition and concentration of SBF solutions to produce a favorable HA/calcium phosphate deposition (61, 62). In contrast, this study was able to demonstrate that the regular SBF solution concentration may be maintained while shortening the length of SBF immersion. To achieve this, surfaces that had little impact on the makeup and shape of the coating were prepared. Additionally, this study demonstrated that an implant surface coating made of a more uniform, thinner layer of HA/tri-calcium phosphate that was submerged in SBF for no more than seven days would be adequate. All of the SBF immersion periods' biomimetic coatings had compositional and structural characteristics that were very similar to those of human bone.

Conclusion:

A crucial clinical problem is the degradation of dental biomaterials. Despite recent inventive developments in metallurgical science and technology as well as impressive advancements in the design and production of surgical and dental materials, failures nevertheless happen. The Department of Dental Research, INMAS, DRDO, has designed and produced domestic base metal alloys and titanium implants. Research has shown that the materials can be utilized to restore oral deformities and are biocompatible with the standards in place. The study's goal is to evalute the corrosion of locally sourced base metal alloys with locally sourced titanium dental implants in vivo settings. This work was effective in demonstrating that applying HA/tricalcium phosphate to titanium surfaces to produce thin, homogeneous coatings is a feasible method. Due to the creation of an oxide layer, titanium demonstrates excellent corrosion resistance; nonetheless, titanium's success as a dental implant material depends on the preservation of this oxide layer. Dental implants with hydroxyapatite coatings offer good corrosion protection. Chitosan-hydroxyapatite coatings showed stronger corrosion protection values than hydroxyapatite alone, encouraging higher stability and homogeneity of chitosan coating.

Declaration of interests:

The authors declare no conflicts of interest.

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