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Surface Characterization of Pure and Composite Sol-gel Nano-coatings Deposited on 316L Stainless Steel for Hard Tissue Replacements

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Coating of stainless steel (SS) plays a crucial role in improving the properties required for various biomedical applications. These characteristics include biocompatibility, mechanical along with corrosion and wear performances. In this respect, this study developed uniform pure hydroxyapatite (HA) and HA/ titania (TiO_2) composite films applied on the surface of SS using the sol-gel technique. The morphology and chemical composition of investigated surfaces were analyzed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. Moreover, uncoated and coated SS substrates' surface roughness, micro-hardness, and wear characteristics were evaluated. The results displayed that a homogeneous nano-scale surface with higher values of micro-hardness and wear resistance is obtained for coated SS substrates, especially for HA/TiO_2 composite coating.

Keywords: *316L stainless steel, coating, hard tissue replacements, nanocoatings, nanocomposite film.*

1. Introduction

As is well known, metallic alloys like cobalt-chromium, titanium-based alloys, 316L stainless steel (SS), and others are essential engineering biomaterials. These materials are used for different biomedical applications, especially hip joint prostheses and dental implants, due to their outstanding thermal conductivity and mechanical properties. SS is one of the most important materials used for different areas of bioimplants due to its satisfactory combination of mechanical characteristics, corrosion behaviour, and reduced cost compared to other biomaterials[1]. Among SS kinds, 316L SS is the most widely implanted material in the human body. It is extensively utilized for dental field, bone fracture-fixation, and joint replacements because of its distinctive properties such as mechanical performance, biocompatibility, corrosion behaviour, and producibility[2,3]. The osseointegration may be affected by the surface characteristics of 316L SS implants and the biological response at the interfaces between these implants and the surrounding tissues[4]. However, several biological complications, such as inflammation, allergy, corrosion, wear, etc., can be induced owing to the reverse interaction of the implants with the body tissues. Therefore, surface modification of 316L SS is greatly required in order to overcome such difficulties. Applying bioactive ceramic film on the metallic surface is a vital solution to improve the surface characterization of metallic biomaterials. It is important to control the major parameters of material's coating process as they may highly affect on the required morphology, phase structure and distinct physicochemical characteristics[5].

Consequently, various surface coating/modification techniques have been extensively applied on the surface of various biomaterials. These techniques include chemical vapour deposition (CVD), anodic oxidation, micro-arc oxidation (MAO), plasma spraying, electrostatic spray deposition (ESD), electrophoretic deposition (EPD), pulsed-laser deposition (PLD), sol-gel and others. The sol-gel is one of the greatest, simple and cost-effective techniques of surface modification[6] to produce various thin oxide coatings, in case of single or multicomponent film, onto glass or metallic substrates[7]. Sol-gel-derived ceramic films are usually used as protecting layers against tribological and electrochemical reactions of different engineering metallic substrates. This process is accomplished at a relatively lower temperature compared to other conventional coating approaches. In recent years, different coating materials like ZrO_2, Al_2O_3, ZrO_2/Al_2O_3, hydroxyapatite (HA), TiO_2, Ag/TiO_2, Ti/HA, HA/TiO_2, etc. were applied onto different medical surfaces as a result of their similarity with the inorganic constituents of the body structure. Among them, HA is a favourable bioactive ceramic since it has very close characteristics to human bones, especially structural, chemical, and biological, increasing its capability to bond strongly with surrounding tissues[8]. Also, it was reported that HA-coated implants display superior corrosion resistance compared to uncoated implants[9,10]. Dip-coating and spin-coating are the most widely used methods for the preparation of HA and other films on SS implants. In this regard, Jonauske et al.[11] conducted a practical comparison of the quality of the coating produced on the SS surface and its properties resulting from the use of these two methods. The authors pointed out that these techniques are highly effective methods of depositing HA coating on the surface of SS with a preference for using the spin-coating technique. However, HA has weak mechanical performance and poor adhesion of to the surface of SS which may lead to restrict its application in different load-bearing applications such as hip and dental implants. All these drawbacks still represent a great challenge in the field of medical applications. To accomplish this issue,

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the incorporation of various bioceramic reinforcements into HA matrix is an imperative technical solution to produce biocomposite coating. This could enhance the chemical stability[12] along with the mechanical and bonding strengths of the resulted coating compared to apitite structure[13-15]. Titania (TiO_2) is an outstanding metallic oxide based nanomaterial and promising candidate for various applications owing to its great properties like chemical stability, cost-effective photocatalytic activity and non-toxic nature[16]. It was reported that this kind of coating has significant characteristics such as biocompatibility, cell adhesion[17], bioactivity and bone growth, bonding strength, as well as corrosion resistance[18,19]. Consequently, composite HA/TiO_2 can be considered as a proper coating for modifying the surface of 316L SS[20,21]. In this work, different ceramic coatings were successfully deposited on 316L SS substrate by spray pyrolysis deposition technique. It is expected that this technique may give different results for the structure and properties of the resulting film compared to the other more common sol-gel methods mentioned above.The study of deposition of various nano-ceramic films, especially nanocomposite film, on the surface of 316L SS implants is still limited. The main goal is to investigate the effect of surface coatings on the morphology, topography, wettability, micro-hardness, and wear properties of 316L SS.

2. Materials and Methods

This work used stainless steel 316L (SS) substrate with a surface area of 2 cm^2 as the main surface for the sol-gel process. Firstly, substrates were grinded by silicon carbide papers (180-1000) and then polished with diamond paste (5 μm) so as to get a mirror surface without cracks or scratches. Afterward, the substrates were ultrasonically washed with acetone for 15 min. HA sol was prepared firstly by solving 4.41g from calcium nitrate tetrahedral ($Ca(NO_3)_2.4H_2O$, HIMedia Laboratories Pvt. Ltd, ~99% purity) in 100 ml of methanol (CH_3OH, LAB-SCAN analytic sciences, ~99.8% purity). Then, the gradual addition of phosphoric acid (H_3PO_4, HIMedia Laboratories Pvt. Ltd, ~ 87% purity) drops was made under high-speed stirring to obtain chemical homogeneity using a magnetic stirrer. After one hour of stirring the mixed solution at room temperature, a transparent solution was attained. Consequently, this transparent solution was left for 24 hours to be used for the sol-gel process. Nanopowder solution (CAS# 13463-67-7) of 20% TiO_2 (30-50 nm) was utilized to prepare a solution for HA/TiO_2 film. Initially, the nanopowder solution was mixed with water for 10 min by ultrasonic mixing. Then, the prepared solutions of HA and TiO_2 were carefully mixed together and constantly stirred for 6 hours using ultrasonic mixing to obtain a composite solution consisting of 80 Vol.% of HA and 20 Vol.% TiO_2. It is vital to mention here that the PH of solutions used in the coating process was adjusted to PH 9 by adding NH_4OH. Finally, HA and HA/TiO_2 composite films were deposited onto the surface of SS substrates by spray pyrolysis deposition, followed by thermal treatment. Firstly, many SS substrates were heat treaed at 100 °C to evaporate the organic compounds in the precursors used during the process. The prepared HA and HA/TiO_2 solutions were then pumped on the surface of substrate using specific nozzle at 2 bar for 10 seconds. Air drying for 15 min was then made, followed by thermal treatment at 550 °C for 1 h with a heating rate of 5 °C/min. Eventually, the attained films were cooled in furnace to room temperature. More details were described elsewhere[22].

The surface morphology and composition of the deposited films were examined using scanning electron microscopy (SEM-FEI Quanta model, Holland) and energy dispersive spectroscopy (EDS) attached to the SEM device. A digital thickness gauge (List-Magnetik Mega-Check Pocket; an accuracy: ± 0.1μm) was utilized to measure the thickness of deposited films by computing the average of five measurements at different surface points. AFM device (NTMDT, NTEGRA prima, Russia) was used to determine the topography (2D and 3D images) and partial size of the investigated 316L SS surfaces. Wettability of the uncoated and coated SS substrates was estimated by measuring water contact angles using optical contact angle and interface tension meter model SL200KS. The test was carried out in ambient atmospheric environments using three drops of ultra-pure distill water at different areas for each substrate. The micro-hardness test was carried out for uncoated and coated 316L SS using a Vickers tester (TH715, Beijing Time High Technology Ltd) at a load of 9.8 N and a dwelling time of 15s. Note that the test was repeated at least five times for each surface.

A reciprocating pin-on-disk sliding wear tester (MICRTEST, S.A., Spain) was utilized to evaluate the wear resistance of uncoated and coated SS substrates at room temperature. The wear test parameters were chosen to be 1N for applied force, 200 rpm for sliding velocity, 6 mm for pin diameter, and 75 m for sliding distance. The coefficient of friction (COF), and wear rate were determined depending on the applied load and the recorded friction force.

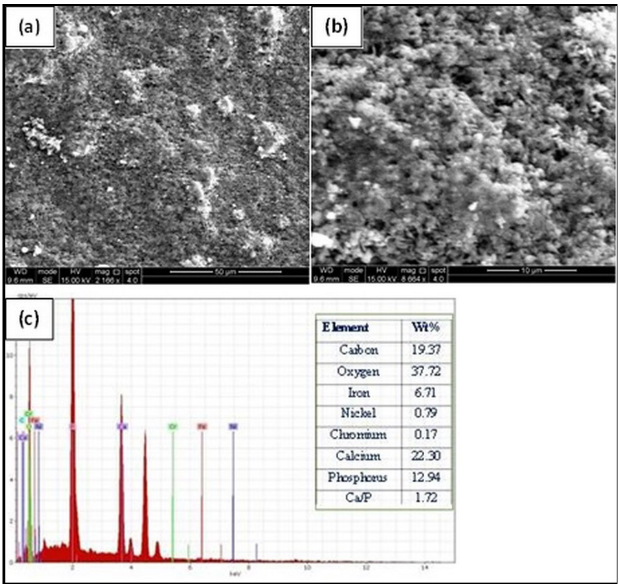
3. Results and Discussion

Controlling the structural morphology and composition of the coatings processed by sol-gel, greatly affects the performance in hard tissue applications. From this point of view, the influence of these coatings on the required characteristics of the of the implant's surface should be evaluated. This study applied a high focus on HA and composite HA/TiO_2 ceramic coatings due to their great chemical and thermal stability. Thus, various required characteristics of the coatings created by sol-gel may significantly depend on the surface morphology along with the nature of the materials utilized in this coating process

Firstly, the visual inspection of the coated substrates was achieved, and it was noticed that the processed substrates are completely coated with these films in high homogeneity. Figures 1a & 1b exhibit different magnifications of SEM micrographs for pure HA film. It can be seen from this SEM observation that no noticeable surface cracks are detected in the surface coated by HA film. The pure HA film consists primarily of nano-particles, coarse-particles, and large grains in an irregular distribution. The individual particles are almost (150–350) nm in size. Moreover, internal voids and plentiful micro-pores of (1-3 μm) size were also detected within the structure of pure HA film, developing a sponge-like porous structure. It was reported that these pores are produced in the coating due to the gas evolution during thermal pyrolysis of residues[23]. It is vital to mention here that this porous layered structure may develop the performance of an implant with higher biofunctionality.

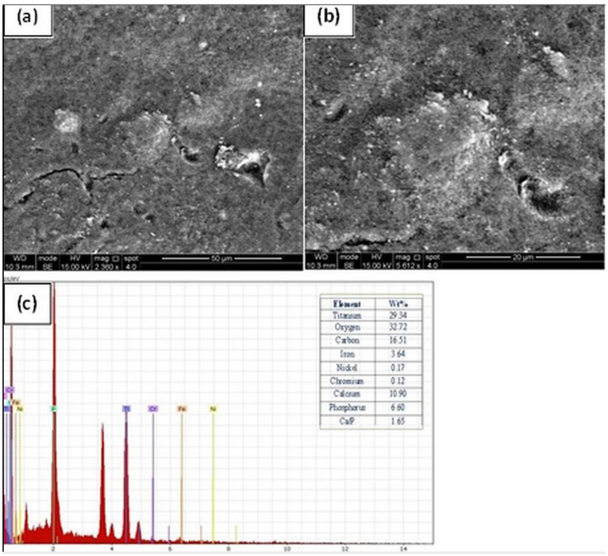
The movement of body fluid through the pores may promote the cell infiltration process and the development of new bone cells. Moreover, the formation of porous structures in bioceramic films significantly affects osteoblast adhesion and differentiation by inducing more attachment points[24]. Figure 1c presents the corresponding EDS spectra of HA film. The figure shows the presence of intense peaks of the main elemental composition of Ca and P, which approves the formation of HA film. This means that the apatite (HA) layers were successfully formed on the surface of SS substrate. Moreover, the Ca/P ratio of deposited HA film is 1.72 which is slightly higher than the actual value (1.67) in bone structure. Some peaks related to the SS elements, i.e., Fe, O, C, and Ni, were also noticed.

Figures 2a & 2b show the surface morphology of HA/TiO_2 composite film in low and high magnification. As seen, the surface of the deposited composite film has a homogeneous, uniform, and dense structure in appearance with a limited porous network. In other words, the surface of the composite film contains nanoparticles with regular spongy structure in a less porous amount and greater homogeneity and uniformity. Same surface regularity of the composite film has been reported by[25].This may be associated with the higher incorporation of TiO_2 with the HA matrix. The surface has a substantial reduction in the dimensions of pores (1-1.5 µm size) compared to that of HA film. Also, the dense structure of composite film is an effective factor for increasing the mechanical properties especially the fracture toughness[26].



Element	Wt%
Carbon	19.37
Oxygen	37.72
Iron	6.71
Nickel	0.79
Chromium	0.17
Calcium	22.30
Phosphorus	12.94
Ca/P	1.72

Figure 1. SEM images of pure HA film at (a) low magnification, (b) high magnification, and (c) point EDS spectrum.



Element	Wt%
Titanium	29.34
Oxygen	32.72
Carbon	16.51
Iron	3.64
Nickel	0.17
Chromium	0.12
Calcium	10.90
Phosphorus	6.60
Ca/P	1.65

Figure 2. SEM images of HA/TiO_2 composite coating at (a) low magnification, (b) high magnification, and (c) point EDS spectrum.

It can be concluded that HA/ TiO_2 composite film sounds optimal with the desired surface properties compared to the HA film. Figure 2c shows the EDS spectra of the HA/TiO_2 film. The presence of clear peaks for Ca and P in company with Ti and O peaks approves the development of HA and TiO_2 in the composite film, respectively. This confirms that the TiO_2 phase was well embedded into the HA matrix and the composite film has higher purity. Furthermore, the Ca/P ratio was measured to be 1.65 which is closer to the theoretical value of Ca/P in human bone. Minor peaks corresponding to Fe, C, Cr, and Ni were also detected in the SS.

Figure 3abc displays the AFM images of the uncoated, HA, and HA/TiO_2 composite films deposited onto the surface of SS substrate. The typical images of the AFM test are presented here, along with values of mean root square (RMS) roughness determined in three diverse free-macro defect areas on the deposited films. Figure 3a showed that the uncoated SS surface has a lower RMS (74 nm) compared to the coated surfaces. This reveals the substantial influence of various films created by the sol-gel technique on the roughness of SS substrate. On the other hand, the test exposed that the coated SS surfaces are entirely coated with nano and rough coatings. The topography of HA film revealed the development of nanoparticles (99.5 nm grain size) within this surface, as shown in Figure 3b. Also, this film illustrates a porous structure with a higher RMS (108 nm) than that of an uncoated substrate. The surface roughness of this film is highly connected with the formation of large zones of agglomeration and porosity along with reduced uniformity, as shown in Figure 1. In the case of HA/TiO_2 composite film, AFM analysis (Figure 3c) disclosed that TiO_2 is greatly incorporated with HA. Moreover, a homogeneous nanostructure with reduced particle size (70.5 nm) is attained in the composite film. Also, the surface of the composite film has reduced amounts of porosity compared to HA film. The RMS roughness value of the film (RSM= 97.6) is evidently lesser than that of HA but still higher than that of uncoated substrate. This decrease in the surface roughness of composite film is attributed to the the higher uniformity of the composite film as a result of the increase of TiO_2 concentration in the HA matrix[14,25]. It should be noted that the increased surface roughness is an effective factor for enhancing the rapid attachment of the osteoblast cells onto the implant surface, which could substantially improve the entirely interaction area with the bone[27]. Consequently, it is anticipated that the coating process in this work has an essential effect for developing the capability of bone-bonding and bioactivity.

It is well recognized that any biomaterial used as a load-bearing implant for a long period in the human body must have advanced mechanical and biological characteristics due to the intricate nature of the human body fluid. Hence, in the present work, the micro-hardness analysis was accomplished as a crucial mechanical property for coated surfaces. Also, the thickness of the film is a vital parameter that could significantly affect the performance of SS implants coated by spray pyrolysis deposition. It is well identified that the best thickness for biocoating is less than 100 μm to achieve an optimal value that applicable to orthopaedic implants. Hence, in this work, the values of coating thickness for HA and HA/TiO_2 films (19 ± 1.5 and 26 ± 3.7, respectively) are appropriate for these medical applications. Moreover, the suggested coating thickness values (< 100 μm) promot the best bone growth and osseointegration[28]. The micro-hardness and the thickness results for uncoated, HA and HA/TiO_2 coatings are shown in Table 1.

Table 1. Micro-hardness amd thickness values of uncoated and coated SS substrates

SS Sample	Thickness (μm)	Micro-hardness (HV)
Uncoated	-	277±2.5
Pure HA	19 ± 1.5	361±1.8
Composite HA/ TiO_2	26 ± 3.7	469±2.6

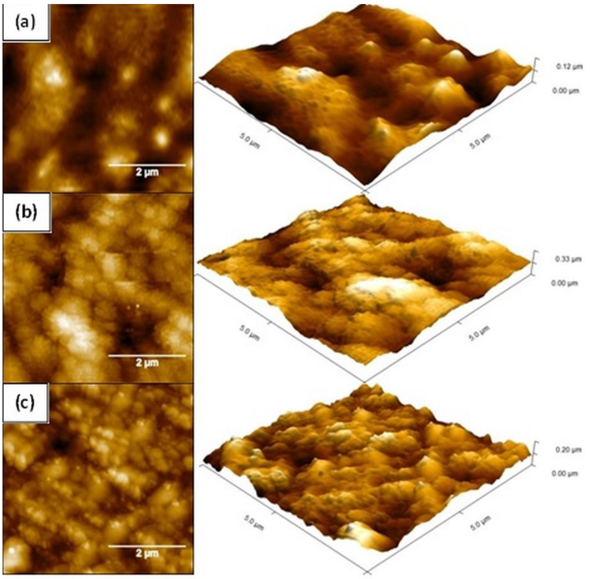


Figure 3. AFM images of investigated films: (a) uncoated, (b) HA, and (c) HA/TiO_2.

It is important to mention here that the the morphology of the coated surfaces is an affected parameter on the micro-hardness values. The uncoated SS surface showed the lowest value of micro-hardness (277±2.5 HV) compared to coated SS substrates. Furthermore, HA/TiO_2 composite film displayed the highest hardness value (469±2.6 HV) compared to pure HA (361±1.8 HV). Therefore, HA/TiO_2 surface film offered the optimum value for surface micro-hardness since this coating has a dense structure in higher homogeneity, inferior amount of porosity with better incorporation of TiO_2 with HA matrix (see Figure 2a & 2b). For the composite film, the addition of TiO_2 in HA matrix could develop the physical reliability between the deposited film and the substrate along with increasing the inter-particle interaction[29]. Subsequently, this may lead to a significant increase in the surface hardness. Furthermore, the development of the nano-scale film in composite film, without any apparent micro-cracks or detachment from the substrate, is an essential outcome that may cause an increase in the bonding strength of this film onto the SS surface.

The influence of the produced coatings on the hydrophilic properties of SS base substrates was estimated by measuring their water contact angles and comparing them with that measured on the base SS substrate, as shown in Figure 4. This figure indicates that there is an obvious improvement in the surface wettability after sol-gel coatings. The contact angle measurements of SS substrate present the highest value (75.9° ± 0.2 deg), whereas the coated substrates exhibited the lowest contact angles (41.7° ± 0.1 deg and 22.5° ± 0.7 deg for HA and HA/TiO_2 composite films, respectively). This means that the coated SS substrates' wettability was significantly higher than the as-received SS surface. Moreover, the droplet contact angle of the substrate coated with HA/TiO_2 composite film was the lowest value, confirming the best wettability and the highest hydrophilicity of this coating owing to the presence of hydroxyl on the surface of coated film.

It is well known that friction and wear of implantable materials are very important concerns as a result of inverse outcomes coming from the direct implant contact with surrounding tissues. Hence, wear debris in the contact area may cause several biological problems like bone loss, inflammation, and cytotoxicity[30]. At first, through the visual inspection, it was noticed during the wear test that the amount of broken and crushed particles on the surface of the uncoated SS substrate was greater compared to the coated substrates. Figure 5 displays the coefficients of friction of uncoated and coated SS substrates. The average values of the friction coefficient of uncoated, HA, and HA/TiO_2 films were 0.88, 0.74, and 0.49, respectively. The figure indicates that a constant increase in the COF occurred after increasing the time of the wear test for all tested substrates. This increase in COF may be induced as the result of the formation of wear particles during the continuity of the test, which may cause abrasive wear with the possibility of failure of the surface film[31]. In addition, the values of COF for coated SS substrates were considerably lower compared to that of uncoated SS substrates. However, pure HA has an inferior effect on developing the wear resistance of SS surface due to the weak interface between this film and the SS surface. This also may be attributed to the microstructural features of this film (see Figure 1a & 1b). Consequently, it is expected that the interface's micro-fracture may occur along with the accumulation of wear particles, which could eventually lead to the rapid failure of HA film. On the other hand, HA/TiO_2 composite film has the lowest COF value, reflecting its higher wear resistance and longer wear life. This may be related to the outstding surface properties of this type of nano-scale structure coating in terms of perfect structure stability, homogeneity, and uniformity, and the high surface bonding between HA/TiO_2 film and SS surface without inducing any dilapidation or peel-off of the film. (see Figure 2a & 2b). Besides, the substantial decrease in COF of the HA/TiO_2 film may be related to the significant enhancement in some important surface properties like structure stability, film thickness, surface hardness[32], and roughness[33,34]. In the same way, the wear rates of uncoated, HA, and composite films were determined as shown in Figure 6.

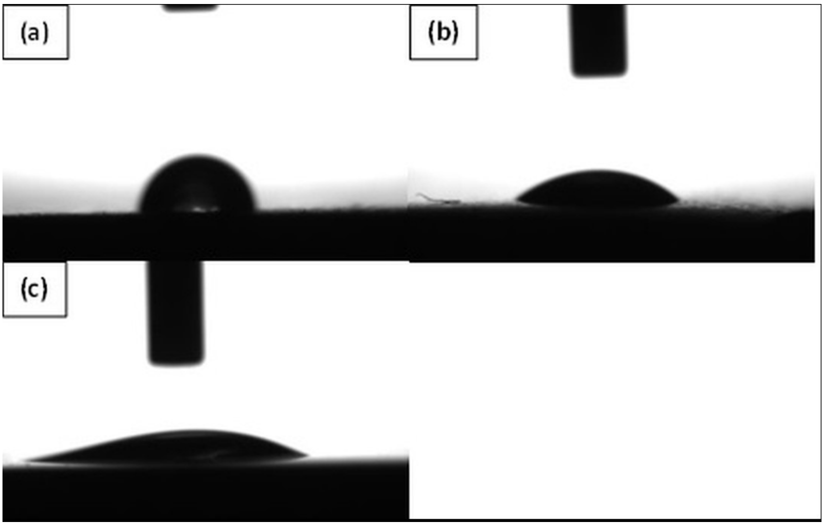


Figure 4. Optical images of water contact angles of (a) uncoated, (b) HA, and (c) HA/TiO_2.

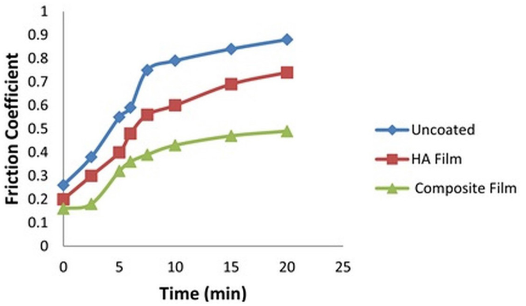


Figure 5. Coefficients of friction of uncoated, HA, and HA/TiO_2 composite coated SS substrates.

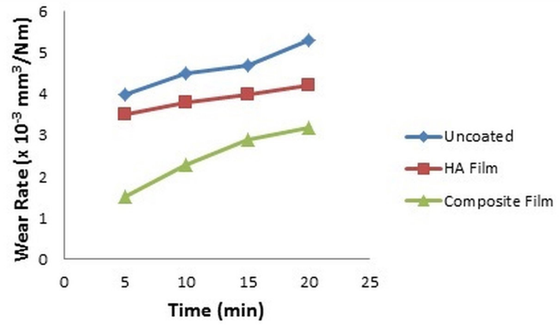


Figure 6. Wear rates of uncoated, HA, and HA/TiO_2 composite coated SS substrates.

Here, the uncoated substrate has the highest value of the wear rate comparing with the coated substrates. Also, the composite film shows the lowest wear rate value compared to HA coated substrate. It is important to note that the ceramic coatings in nano-scale show some plastic deformation even at room temperature[35]. Hence, the nanostructure of composite film (Figure 2a & 2b) may induce plastic deformation. The deformation is so probably responsible for prevention or decrease the potential creation of micro-fractures, which could lead to a significant decrease in friction coefficient and abrasive particles. In summary, we can conclude that the results of wear rates are quite close to the results of COF, with the possibility of including the same reasons in the analysis of the results.

4. Conclusion

In this work, deposition of pure HA and HA/TiO_2 films on 316L SS substrate was successfully performed by spray pyrolysis deposition technique. The synthesized films' structural morphology, thickness, topography, micro-hardness, and wear properties were investigated. Findings attained from the experimental procedures can be summarized as follows:

1. Crack-free films of pure HA and composite HA/TiO_2 with a porous structure were successfully synthesized by spray pyrolysis deposition on the SS substrate.
2. Nanosized particles, along with coarse particles and large grains in an irregular distribution, are the major structural features of HA film. Also, this structure develops a sponge-like porous network owing to the presence of plentiful internal voids and micro-pores.
3. The surface of HA/ TiO_2 composite film has nano-particles with homogeneous, uniform, and dense structures due to the higher incorporation of TiO_2 with the HA matrix. Furthermore, a regular spongy structure with limited porosity is accomplished for the composite film.
4. The composite film presents the highest values for surface micro-hardness and wear properties owing to its advanced nanostructures.
5. Hence, 316L SS coated by spray pyrolysis deposition is a very favourable material for hard tissue replacements.

5. Acknowledgements

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6. References

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