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Original Article

Differential Analyses of Naturally Prepared and Synthetic $CaCO_3/SiO_2$ Composite Implant Coating Material: an *in vitro* Study

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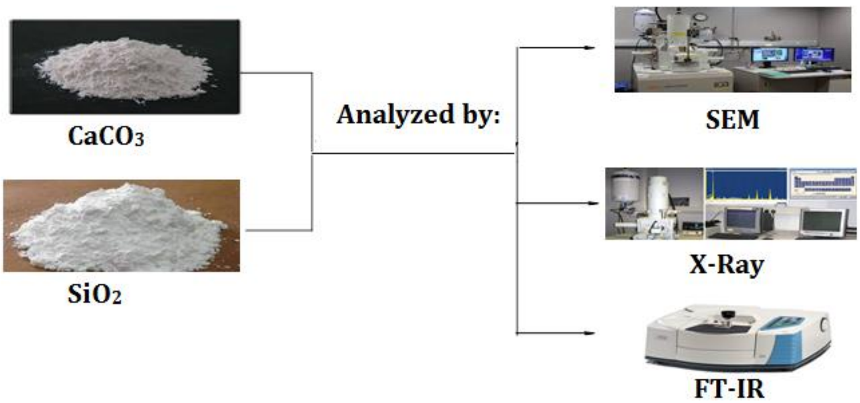
ABSTRACT

This study aims to present the evolvement and characterization of two innovative bioactive coating composite materials overlying Yttria-stabilized tetragonal zirconia substrate. The differential analyses between artificial $CaCO_3/SiO_2$ and novel natural prepared $CaCO_3/SiO_2$ composite implant-coating material.

The methodology of the present study involved forty disc-shaped specimens with a dimension of 10 mm, and twenty disc-shaped samples with 50 mm diameter were prepared from partially sintered Yttria-stabilized tetragonal zirconia polycrystal. The naturally prepared composite was deposited via radio frequency reactive magnetron sputtering**.** The experimental specimens were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), and atomic force microscope (AFM). A wettability test was conducted using the mean of contact angle measurement. Pull-off tests were also performed to assess the adhesion strength between zirconia substrate and the experimental coating materials.

According to the outcomes of the present study, we concluded that the naturally prepared $CaCO3/SiO2$ composite exhibits more hydrophilicity with an improvement in the adhesion force to the zirconia substrate compared to the artificial $CaCO_3/SiO_2$ composite. Therefore, it can be used as a coating material for zirconia implants with promising biological and mechanical properties.

GRAPHICAL ABSTRACT



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Introduction

Dental implants have been extensively used to support prosthodontic restorations, removable and fixed, and maxillofacial restorations, with a high degree of success [1]. Different types of material were used as implants; the most common is titanium and its alloy, and recently zirconia acquired robust interest due to many desirable properties [2]. The materials above, titanium, and zirconia are regarded as bioinert materials that necessitate the use of bioactive material, a coating overlying the bioinert substrate [3]. The selection of the bioactive coat depends on physicochemical characteristics and the availability and affordability of the material. Natural biocomposites recently received widespread attention as an active coating covering metallic implants due to their bioactivity, availability, and affordability [4]. Micro-nano organizational amendment of the implant's surface may improve bone conductivity and hydrophilicity and decrease the conducted stress [5]. Calcium oxide/silicon dioxide-built bioceramics have been considered probable alternatives for artificial bone due to their excellent biocompatibility and Osseoinductivity [6]. In recent years, employment of by-products or leftover agricultural operations received a wide broad consideration in emerging technologies, scientific pursues, and biological scopes [7]. Rice husk is an agricultural residue material plentifully available in Iraq and rice-producing countries. Rice husk ash is rich in silica and can manufacture silica powder [8]. Several authors reported that the rice husk ash was an exceptional resource for amorphous silica [9, 10]. Chicken eggshell agricultural junks represent the environmental pollution problems. The chemical composition of eggshells is composed mainly of calcium carbonate $CaCO_3$ [10]. Eggshell is regarded as massive pollution for the environment. Ais regarded as massive pollution for the environment and a rich source for $CaCO_3$ and CaO, making the opportunity to utilize eggshell as an alternative sustainable source for bioactive osteoconductive material [11]. This study aims to characterize and differentially analysis between artificial and novel natural prepared calcium carbonate ($CaCO_3$)/ silica SiO_2 composite as a bioactive implant-coating material.

Materials and Methods

Smaple Preparation

Disc-shaped specimens with a dimension of 2 mm thickness and 6 mm diameter were prepared from partially sintered Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) (Vita, Zahnfabrik H. Rauter GmbH & Co., Germany) substrate using Exocad dental computer aid design/computer aid manufacture (CAD/CAM), Imes Icore CORiTEC 250i, Germany [12]. The specimens were sintered with Vita ZYRCOMAT 6000 MS sintering furnace showed in, 40 specimens with 10 mm diameter (10 specimens for each test) were recruited for x-ray diffraction (XRD) (Lab X, XRD 6000, SHIMADZU, Japan), field emission scanning electron microscope (FESEM) (Inspect f50 FE-SEM; Netherland), energy-dispersive X-ray spectroscopy (EDX) (Bruker, Italy), X-ray fluorescence (XRF) (PAN analytical laboratories, Tehran, Iran.) and atomic force microscope (AFM) (ICAN, Iran). Other twenty specimens were fabricated in a disc with a diameter of 50 mm specific for adhesion and wettability tests [12,13]. The specimens were divided into two groups; in the first group, the Y-TZP specimens were coated with a natural prepared $CaCO_3$/ SiO_2 composite. In the second group, the specimens were coated with artificial calcium carbonate ($CaCO_3$)/ silica SiO_2 composite (Silica; Thomas Baker PVT. Limited Mumbai, India 141891.

Calcium carbonite; Thomas Baker PVT. Limited Mumbai, India 29946).

The natural composite coating comprises two natural bioactive ingredients; 90%Wt avian eggshell-derived calcium carbonate and 10%Wt rice husk-derived silica. It had been prepared as recommended by Kareem and Naji in 2021 [10]. $CaCO_3$ was derived from chicken eggshell as follow; the eggshell had been crushed and pulverized with water in ball milling resulting in the slurry mixture, dehydrated at 105 °C for 24 h producing a fine powder which soaked in 50% Sodium Hypochlorite for 10 min then rinsed with water copiously and desiccated at 105 for 1 h followed by pulverizing until the powder passed through a sieve no. 230. On the other hand, silica was derived from Iraqi rice husk as described; the rice husk was crushed, washed, and dehydrated at 105 for 70 °C, then leached with 1 M hydrochloric acid for 2 h at 90 °C and rinsed with deionized water copiously till reach neutralization. The resulted mix was calcinated at 700 °C for 2 h then mixed with 1.5 M NaOH for 1 h at 90°C to produce sodium silicate solution, which mixed with 99% ethanol then water with stirring for 10 min followed by titration with 3 M orthophosphoric acid to form a yellowish gel at neutralized PH. The resulted gel was centrifuged, thoroughly washed with warm distilled water, and after drying, calcinated at 550 °C for 30 min [10].

Coating procedure

According to the pilot study, 20 g of the mixture of calcium carbonate/silica (ratio of 90/10 % by weight) powder was prepared and pressed via cylindrical stainless-steel mold with a dimension of 51 mm diameter and 7 mm height to reduce the porosity and vacancies between the particles and to produce a disc-shaped specimen with a diameter of 50 mm and thickness of 4 mm. Then, the discs were sintered at 900 °C for 6 h to reach sufficient toughness to resist fracture during sputtering [14].

The bioactive composite was deposited on Y-TZP substrate through radiofrequency reactive magnetron sputtering utilizing $SiO_2/CaCO_3$ as a sputtering target. The composition of reactive gas is composed of argon as the sputtering gas. The base pressure in the vacuum chamber is 1×10^{-5} Torr, and the working pressure was 6×10^{-3} Torr. The distance between the target and substrate was 10 cm, and the time of deposition was 20 h at 150 °C and at a frequency equal to 13.56 MHz. [15].

Structural characterization and physical tests

Field emission scanning electron microscope (FE-SEM) is an essential microstructural analysis technique to evaluate the compounds' characteristics [16]. In the present work, FE-SEM with an accelerating voltage of 10–20 Kv was used to reveal the microstructure of the experimental biological coat, including naturally prepared rice husk-derived silica and eggshell-derived calcium carbonate composite. FE-SEM was used to diagnose the phases distribution of particles as well as to characterize the morphology of the prepared specimens

[17]

Energy dispersive X-ray (EDX) spectroscopy was utilized for elemental identification by calculating the number and X-ray energy emitted from the sample after excitement with an electron beam [18]. EDX spectroscopy was conducted in the Technology University/ Department of Applied Sciences.

X-ray fluorescence (XRF) data were analyzed to characterize the elemental composition of the coated zirconia substrate [19]. The XRF analysis of the coating composition was accomplished at Arya electron optic LTD for advanced scientific and industrial equipment, North Shiraz Ave, Tehran, Iran**.**

Atomic force microscope, a very-high-resolution type of scanning probe microscopy (SPM) was utilized for the determination of the 3-dimensional topographies of the surface to investigate the distribution of the atoms (Figure 1) [21].

The wettability of the specimens was assessed through static contact angle measurement using a contact angle goniometer device (Si-plasma CAM 110, creating nanotechnologies, Taiwan) in adjunctive to The Drop Image Software linked to the goniometer, and provides the angle measurements [20].

All the coated specimens were then subjected to adhesion testing (pull out test) (Lasting adhesive tester, Posi Test AT-M AT09442) to assess the adhesion bond between the composite and zirconia disc.

Results and Discussion

Phytochemical Investigation

In this study, the results XRF analysis of coated specimens indicated a significant quantity of CaO, which referred to the presence of $CaCO_3$, which is the main component of the coated composite as listed in Table 1. The cross-section FE-SEM pictures of the coated zirconia specimens exhibited an average thickness of the artificial $CaCO_3/SiO_2$ coat layer that may reach 9.969 µm.

While the natural $CaCO_3/SiO_2$ coat layer may reach to12.84 µm as shown in Figure 2. The increased thickness of natural composite may be attributed to the high cohesion bonding between its particles**.** The coating surface microstructure of natural $CaCO_3/SiO_2$ on zirconia substrate exhibited more porosity than artificial $CaCO_3/SiO_2$, as illustrated in Figure 3. This might be due to increased thickness or may be attributed to the size of particles of the natural composite**.**

Table 1: XRF Elemental analysis of coated zirconia substrate

Element	wt %	Element	Ppm
SiO_2	4.255	S	1276
Al_2O_3	0.198	Cl	509
Fe_2O_3	N	Ba	32
CaO	45.5	Co	N
Na_2O	0.121	Cr	N
K_2O	N	Cu	17
MgO	0.213	Mo	N
MnO	0.013	Nb	115
TiO_2	0.018	Ni	14
P_2O_5	>40%	Pb	107
LOI	3.18	Rb	46
SO_3	3.0972	Sr	116

EDX had been used to support the findings FE-SEM images [23]. The spectra of uncoated specimen postulated the constituent of Zr, Y, O. While the spectra of both coated groups, artificial and natural $CaCO_3/SiO_2$ indicated the content of Zr, Y, O, Ca, and C. as presented in Figure 4. The outcomes of chemical analysis are presented in Table 2 and 3.

Table 2: EDX results for the substrate coated with natural $CaCO_3/SiO_2$

Element	Mass (%)	Atom (%)
Zirconia	60.65	27.29
Carbon	21.28	22.3
Calcium	15.1	39.64
Oxygen	2.85	9.97
Silicon	0.11	0.17
Total	100	100

Table 3: EDX results for the substrate coated with artificial $CaCO_3/SiO_2$

Element	Mass (%)	Atom (%)
Zirconia	0.94	0.19
Carbon	39.11	59.62
Calcium	40.08	18.31
Oxygen	18.13	20.75
Silicon	1.75	1.14
Total	100	100

The EDX maps of coated specimens for both coating materials (natural and artificial $CaCO_3/SiO_2$) demonstrated the excellent distribution of Ca, C, Si, and O as demonstrated in (Fig. 5 and 6). The XRD analysis of the coated zirconia substrate is illustrated in Figure 7. The data acquired from the XRD pattern is identical with the diffractogram of the natural rice husk-derived silica/eggshell-derived $CaCO_3$ composite powder proved by Kareem and Naji in 2021 [10]. Atomic force microscope images in Figures 8 and 9 display representative 2D and 3D surface images for artificial and natural coated specimens, respectively. The images expressing the color bar represent the average surface roughness (Ra) values. The color bar ranged from the bottom with a darker shade (blue) to lighter shade of red. The high peaks of the rough surface are represented by the red color, while the valley depth is represented via the blue color, and the in-between colors express the areas between the peaks and valleys. The surface profile images exposed rough areas as specified by the red colors and the color variations were not smooth across the measured area of the coated zirconia [24]. Pull off test was accomplished to evaluate the adhesion of a coating onto the zirconia sample by assessing the minimum tensile stress needed to detach or rupture the coating perpendicular to the zirconia substrate. The attained results of the two groups artificial and naturally prepared $CaCO_3/SiO_2$ presented in Table 4 display the means, standard deviations, and t-test, indicating a highly significant difference between the two groups; artificial and natural $CaCO_3/SiO_2$ coated substrates. The natural $CaCO_3/SiO_2$ exhibits increased adhesion with zirconia substrate more than artificial $CaCO_3/SiO_2$; this intensification may be attributed to the presence of active amorphous silica within the natural composite.

Table 4: Statistical data of pull-off test

Group	Mean(±SD)	t-test
Artificial $CaCO_3$ /SiO_2	133.75 (**±4.3**)	17.54**
Natural $CaCO_3$ /SiO_2	170 (**± 4.1**)	
**p value < 0.0001		

Wettability (hydrophilic property of coat) is regarded as a crucial property because it directly affects the biocompatibility of the coat in the physiological surroundings, enhancing the osteointegration and osteoconduction [25]. Table 5 demonstrates the wettability assessed by contact angle measurement. The mean contact angle of natural $CaCO_3$ /SiO_2 was significantly higher than artificial $CaCO_3$ /SiO_2 ($p < 0.0001$), indicating the more hydrophilicity of the natural composite. The enhancement of hydrophilicity of natural composite may be due to the decreased size of its particles.

Table 5: Statistical data of wettability test

	Natural $CaCO_3$ / SiO_2	Artificial $CaCO_3$ / SiO_2
Contact angle Mean (±SD)	66.969`	80.982
t-test value	18.8**	
** P < 0.0001		

Conclusions

Recently, byproduct and waste management for developing new products has gained immense interest. Within the limitations of the current study, a biological $CaCO_3/SiO_2$ composite was prepared from avian eggshell and rice husk via simple methods to coat the zirconia substrate.

The microstructural, elemental composition, and bonding analysis confirmed the improvement in the adhesion force of naturally prepared $CaCO_3/SiO_2$ composite to the zirconia substrate compared to the artificial $CaCO_3/SiO_2$ composite. The results of the wettability test indicate the more hydrophilicity of the natural composite. Therefore, it can be used successfully as a coating material for zirconia implants with promising biological and mechanical properties.

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Data Availability

The data file of this study is available from the corresponding authors upon reasonable request.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to responsible for all the aspects of this work.

Conflict of Interest

The authors have no conflicts of interest relevant to this article.

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