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Original Article

Enhancement of 316L SS Implants by Nanochitosan-YSZ Composite Coatings by the Dual Method for Dental Applications

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This work provides a concise overview of a novel approach to enhance the performance of 316L stainless steel (316L SS) implants for dental applications. Dental implants have revolutionized the field of restorative dentistry, offering a durable and biocompatible solution for tooth and jaw replacements. However, to further improve their success rate, this study explores the utilization of nanochitosan-Yttria-stabilized zirconia (YSZ) composite coatings on 316L SS implants using a dual-method approach. The dual method incorporates both electrochemical deposition and dip coating techniques for the deposition of nanochitosan-YSZ composite coatings. The study involves a comprehensive investigation of the coating's structural, mechanical, and biological properties. It assesses the adhesion, thickness, and surface morphology of the composite coatings, as well as their corrosion resistance in simulated oral environments. The results of this research demonstrate the potential of nanochitosan-YSZ composite coatings applied via the dual-method approach to significantly improve the performance and longevity of 316L SS dental implants. The findings indicate that this innovative coating strategy has the potential to reduce implant failure rates, enhance patient outcomes, and promote the broader application of 316L SS implants in dental practice. This work contributes to the ongoing advancement of dental implant technology and offers promising insights for future research and clinical implementation.

Introduction

In the dental industry, noble metal-based dental implant materials possess significant effects. Noble material-based dental implants were quite costly, and they are not available for many people at an affordable cost [1]. Dental implants are a common and effective solution for replacing missing teeth. They are essentially artificial tooth roots made of biocompatible materials like titanium and 316L SS that are surgically placed into the jawbone. These implants provide a stable foundation for replacement teeth such as crowns, bridges, or dentures [2]. 316L stainless steel is commonly used for surgical implants such as orthopedic implants, joint replacements, bone screws, and plates due to its biocompatibility and corrosion resistance [3,4]. However, the use of SS as a dental implant has some limitations, as the failure of 316L stainless steel can occur under certain conditions, despite its generally good mechanical properties and corrosion resistance. Failures can result from factors such as stress, environment, temperature, and material defects. [5,6]. The surface of implant materials gets corroded easily in a low-pH acidic medium due to the release of more ions. Thus, innovative techniques like surface modification of dental implant materials with more corrosion resistance and cell proliferation are the need of the hour. Surface modification with nanobiocomposites possesses high tissue compatibility, high resistance to corrosion, chemical resistance, high toughness, resistance to wear, and high flexural strength [7]. The durability of dental impacts is very much affected by the adherence and stability of the substrate coating and coating/bone interfaces [8]. Generally, nanobioceramic Yttria-stabilized zirconia (YSZ) is a ceramic material that is widely used for various applications due to its exceptional

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combination of mechanical, high strength, low thermal conductivity, corrosion resistance, and biocompatibility [9, 10]. The addition of biopolymer chitosan increases the values, such as good attachment and cell viability, etc. For more than a decade, novel advanced biocomposite coatings based on chitosan have been developed for dental applications. Chitosan is a well-known biopolymer that has been utilized for several applications due to its properties such as non-toxicity, osteoconductivity, and very good antimicrobial activity. The coating of chitosan averts the colonization of the bacteria on the stainless steel plate [11,12]. The surface of 316L stainless steel is modified by atomic layer deposition (ALD), chemical vapor deposition (CVD), and physical vapor deposition (PVD), but electrophoretic deposition (EPD) is a suitable method for the deposition of nano YSZ on the surface of 316L stainless steel [13, 14]. The advantages of EPD are its simple and cheap power source equipment, which provides highly uniform and crack-free coating from various alcoholic suspensions with controlled deposition rates by varying the applied voltage and coating time. Due to the marked advantages such as ease in obtaining the desired thickness, formation of layers with high purity, stronger adhesion to the substrate, etc., the EPD method was chosen compared to all other methods. The EPD process is considered an effective technique to develop ceramic coatings on functionally graded materials and on complex-shaped substrates [15,16].

It is reported that nano-YSZ-based dental implants showed high mechanical strength and phase stability at various temperatures [17]. Moreover, nano YSZ, along with a biopolymer chitosan-coated dental implant, would be considered an alternative to conventional dental implants as it provides several advantages, such as accelerating the formation of osteoblasts responsible for bone formation. The main advantages of biocomposite chitosan layers are that they are highly resistant to various ion attacks from artificial saliva and that they also accelerate the formation of osteoblasts responsible for bone formation. The mechanical properties and osteogenic properties of the composites can be improved by adding YSZ to chitosan; however, this improves the mechanical strength and osteogenic properties of the composites.

To the best of our knowledge, the development of nanochitosan/YSZ-based coatings for dental applications is rarely reported. In this work, we report nano YSZ coating on 316L stainless steel by EPD, followed by dip coating of nano YSZ coated samples in chitosan solution. Further, the electrochemical behavior of coated samples was evaluated in an artificial saliva medium for dental applications. Also, the viability of the cells was evaluated in order to confirm their biocompatibility.

Materials and Methods

Nano YSZ (99.99%) (particle size <100nm), Nano Chitosan (degree of deacetylation 100), obtained from Thermo Fischer Scientific. The IPA solvents, acetic acid, and other chemicals used were of analytical grade.

Substrate preparation

ASTM F-89 standard 316L stainless steel (10×10×2 mm size) samples were used as a working electrode after polishing it mechanically using grit silicon carbide papers, followed by a gentle wash in dilution of HCl and soap oil solution. Further, the samples were ultrasonically cleaned and then dried in an oven. The dried 316L stainless steel substrates were stored in desiccators prior to the EPD process.

Nano-YSZ suspension preparation and chitosan solution preparation

2% nano YSZ suspension was prepared by mixing 2 g of nano YSZ powder in isopropyl alcohol. Finally, in order to get an agglomerate-free suspension through the ultrasonication process for about 10 minutes, A 2% chitosan solution was prepared by mixing 2 g of finely ground chitosan flakes in 2% glacial acetic acid. The resultant solution was stirred constantly for 10 hours. The obtained homogeneous solution was stored in a cool place.

Nano YSZ deposition on metal substrate by EPD process

316L stainless steel (10×10×2 mm sized) was used as the working electrode, and a thin plate of 314 SS was used as the anode. A distance of about 1cm was maintained between the two electrodes. The working electrode was covered on one side with non-conducting Teflon tape, and then the covered part was dipped in the 2% nanoYSZ suspension so that only the uncovered substrate facing in front of the anode could be coated. During the EPD process, the YSZ suspension was stirred gently. Deposition was carried out on a 1 cm2 surface area with an applied potential of 70 V at a constant time of 5 minutes. The obtained nano-YSZ coating was gently taken out of the bath and dried at room temperature for 5 minutes, followed by air sintering at 800°C. The structural and morphological properties of the obtained samples were examined.

Chitosan coating on nano-YSZ surface by dip coating

The chitosan solution was freshly prepared, and nano-YSZ-coated 316L stainless steel samples were dipped completely for 1 to 5 minutes. All the specimens were then gently removed from the chitosan bath. The chitosan-coated samples were dried at room temperature.

Artificial saliva (AS) preparation

AS was prepared according to the literature reported. [18] Briefly, $C_8H_8O_3$ (2.00g), $C_8H_{16}NaO_8$ (10.00g), KCl (0.625g), $MgCl_2$. $6H_2O$ (0.059g), $CaCl_2.2H_2O$ (0.166g), K_2HPO_4 (0.804 g), and KH_2PO_4 (0.326g) were mixed together in one liter of distilled water. Finally, the pH of AS was adjusted to 6.75 using a KOH solution.

Characterization

The surface micrographs of nano-biocomosite-coated samples were analyzed using a Leica (model DM 2700M, Germany) optical microscope, and the roughness of nano-biocomosite was investigated using ASYLUM Research, USA (model MFP-3D with AC240TS-R3 cantilevers). An electrochemical workstation (BioLogic SP240) was used to investigate polarization resistance and corrosion rate. The cell viability of all samples was analyzed by the MTT assay method.

Results and Discussion

Coating weight and coating thickness

The coating weight and coating thickness of chitosan on nano-YSZ-coated 316L stainless steel are represented in figure 1. From Fig. 1 (a and b), it was observed that the coating weight and coating thickness increased from 1 to 3 minutes, with a decrease at 4 minutes. It was concluded that after 3 minutes, desorption takes place. This was achieved due to the physisorption of chitosan on nanoYSZ. The maximum weight gain was observed at 3 minutes, with coating thickness varying from 22 to 23 μm. Thus, the results indicate the optimum dip coating parameters.

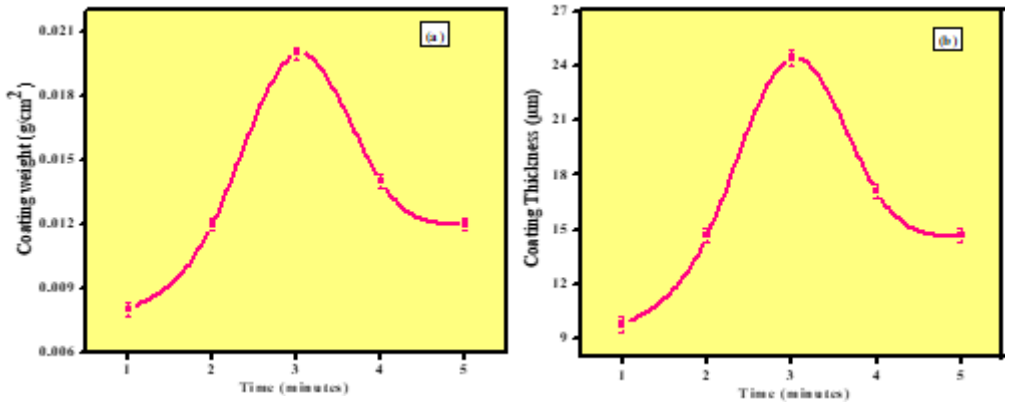

Figure 1: (a) Weight gain and (b) coating thickness of nano biocomposite coated on 316L Stainless steel with respect to time

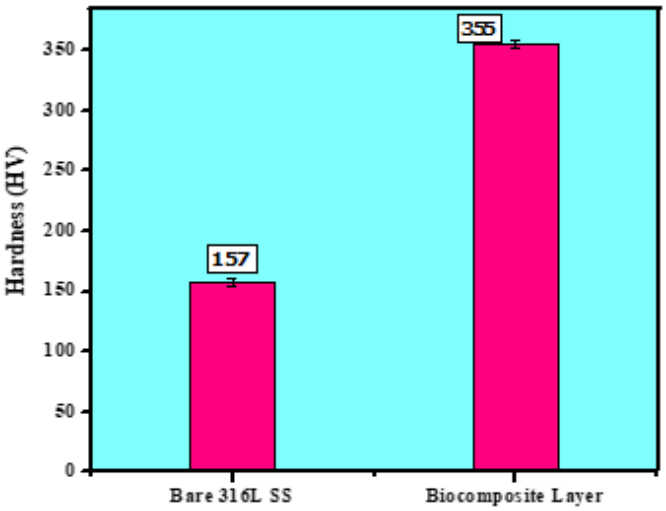

Figure 2: Micro hardness of uncoated 316L stainless steel and nano biocomposite coated on 316L stainless steel

Micro hardness studies

Figure 2 represents the microhardness of uncoated 316L stainless steel and nanobiocomposite coated on 316L stainless steel. To evaluate the stability of the coating, it is necessary to measure the hardness of the coating. The microhardness of the samples (coated and uncoated samples) was measured by applying a constant load of 100 grams. The biocomposite layer possesses a higher hardness value (355 HV) compared to the uncoated specimen (157 HV). The exceptional mechanical strength and stability of the biocomposite layer compared to nanoYSZ-coated and uncoated specimens were revealed by this analysis. [19]

Optical microscopic analysis

An optical microscope was used to study the uniformity and crack-free nature of nanobiocomposite coatings [20]. Figure 3 shows the optical micrographs of nanobiocomposites. It is noted that uniform coating was observed (figure 3 c) only at 2% (w/v) of the chitosan solution. When the chitosan solution concentration is greater than 2%, uniformity is affected, and nano-YSZlayer is peeled off the metal substrate.

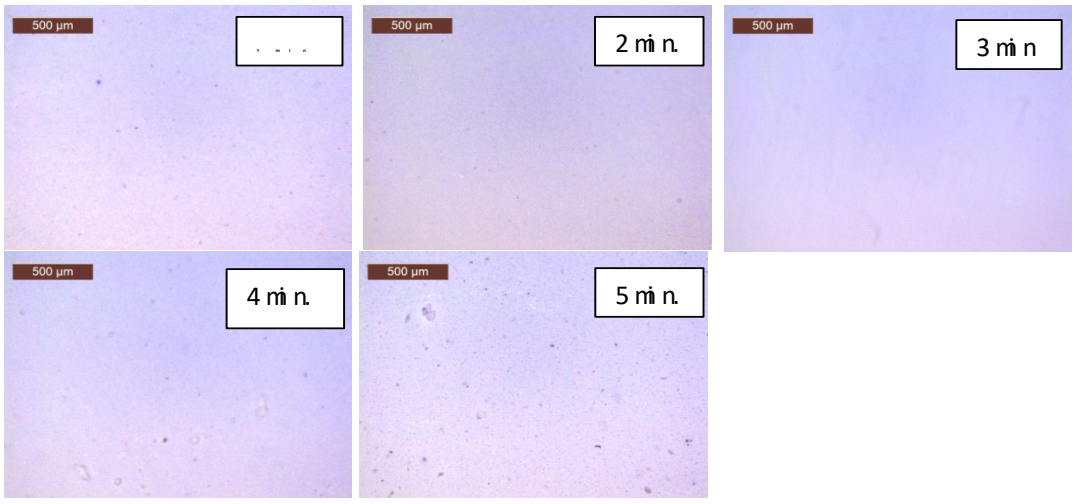

Figure 3: (a), (b), (c), (d) and (e) Optical microscopic images of Nano biocomposite layer coated on 316L SS

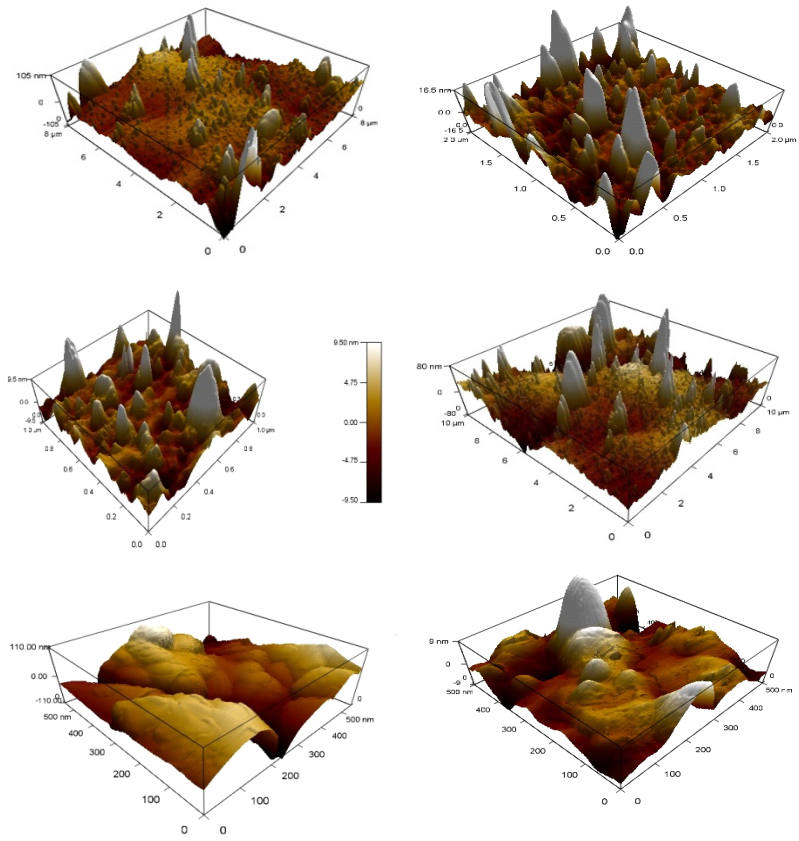

Figure 4: AFM analysis of nano biocomposite coated on 316L Stainless steel

Atomic force microscopic analysis

AFM images of nano-YSZ and nano-chitosan/YSZ were represented in figure 4. AFM analysis confirms the nano-YSZ coating [21] on 316L stainless steel with grain sizes in the range of 50–200 nm and a root mean square surface roughness of less than 10 nm for a 500 nm thick layer, indicating a smooth crack-free surface. The chitosan coated on nanoYSZ by dip coating exhibited a roughness value of 2 nm, indicating a smooth, crack-free surface. The reduction in roughness is due to chitosan passivating on the nanoYSZ surface.

Polarization resistance and corrosion rate

Polarization resistance of nano biocomposite layer on 316L SS and uncoated 316L SS is presented in figure 5. From the figure, it is observed that the polarization resistance increased from 1 minute to 3 minutes and started to decrease at 4 minutes. It is due to decreasing corrosion potential that, as corrosion potential increased, polarization resistance increased, and the rate of polarization resistance decreased. The optimized samples possess higher polarization resistance than other samples.

Table 1: Tafel fit values of nano-biocomposite coated (1-5 minutes) samples in AS medium comparison with uncoated 316L SS

Coating Time	$E_{corr\ (mV)}$ vs SCE	I_{corr} µAcm^{-2}	R_p(KΩcm^{-2})	Corrosion rate mm/year
316L SS	-425	2.308	0.000517	0.0263
1 min.	-105	0.003	22.03009	0.0034
2 min.	-98	0.002	34.24105	0.0027
3 min.	-88	0.001	71.37801	0.0013
4 min.	-110	0.004	15.54218	0.0045
5 min	-115	0.005	11.95874	0.0056

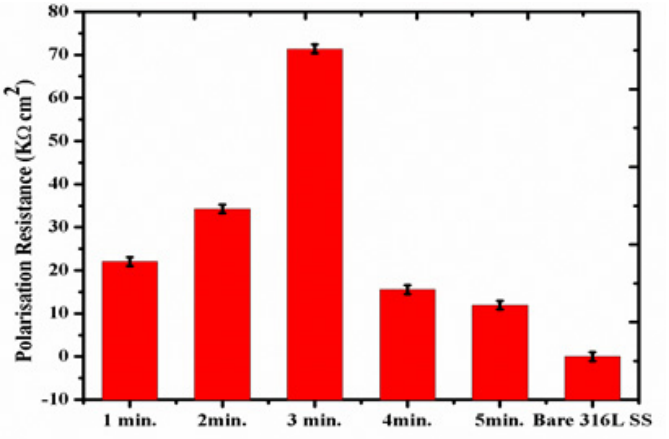

Figure 5: Polarization resistance of nano biocomposite layer coated on 316L SS at 1 – 5 minutes in comparison with uncoated 316LSS in AS medium

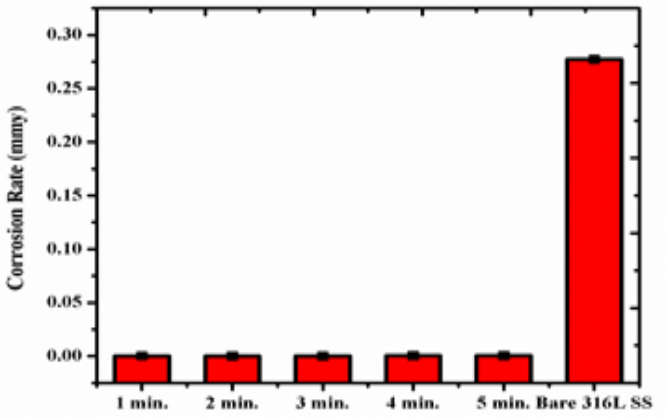

Figure 6: Corrosion rate of nano biocomposite layer coated on 316L SS at 1 – 5 minutes in comparison with uncoated 316LSS in AS medium

Corrosion rate

The corrosion rate of the nanobiocomposite layer on 316L SS and uncoated 316L SS is presented in Figure 6. The corrosion rate was found to be minimum for samples obtained at 3 minutes due to the microfilm-nano biocomposite layer.

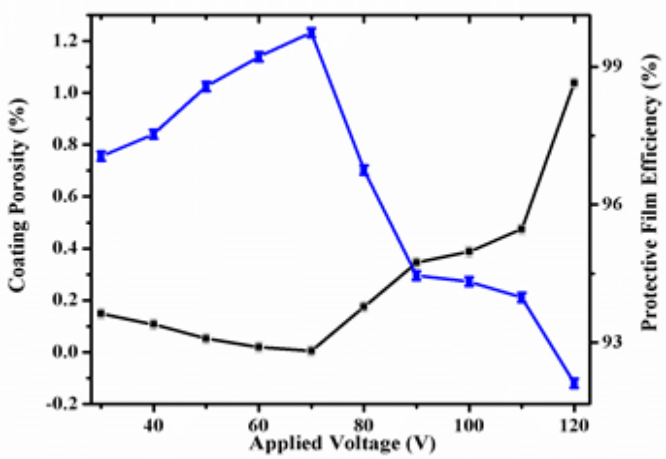

Figure 7: Coating Porosity and protective film efficiency percentage obtained for nano biocomposite coated on 316L SS at 1-5 minutesin comparision with uncoated316L SS in AS medium

Determining the porosity of nano-Zirconia-coated samples is yet another essential parameter for dental applications. The porosity obtained for nano zirconia-coated 316L SS at different coating applied potentials (10–60 V) at a constant time interval of 5 minutes is presented in Figure 7. Porosity values were calculated using the following equation:

$$F = \frac{Rpm(substrate)}{Rp(coating-substrate)} x\ 10 - \left|\frac{\Delta Ecorr}{ßa}\right|$$

where F is the total coating porosity, Rpm is the polarization resistance of the substrate, and Rp is the polarization resistance of the coated steel system. ÄEcorr is the difference in the corrosion potential between the coating and the substrate, and âa is the anodic Tafel slope of the substrate [22].

Protective film efficiency values were calculated using following equation.

$$Ef = \frac{Icorrs - Icorrf}{Icorrs} x100$$

where Ef is the total protective efficiency, $Icorr_s$ is the corrosion intensity of the uncoated steel substrate, and $Icorr_f$ is the corrosion intensity of the coated substrate [23].

The porosity and protective film efficiency of the nanobiocomposite-coated samples are presented in figure 7. It can be seen that the coating porosity increases with the increase in coating applied potential. The low porosity percentage rate of nano YSZ is observed at 70 V and the maximum protective film efficiency.

Biocompatibility studies

The cytotoxicity studies of the uncoated 316L stainless steel nano YSZ and nano chitosan/YSZ coated 316L stainless steel are shown in figures 8 and 9, respectively. This study was carried out using a human MG-63 osteoblast cell line by the MTT assay method. [24,25] The cell viability of uncoated metal, nano YSZ, and nano chitosan/YSZ-coated 316L stainless steel was 75.51, 95.88, and 98.79, respectively. Thus, the cell viability of the nanochitosan/YSZ-coated sample was found to be uniform with a non-porous coating on the metal surface.

Conclusions

Nano YSZ/chitosan uniform crack-free biocomposite coatings were developed on 316L stainless steel by simple, economical EPD and dip coating methods. FESEM and XRD studies confirmed that the nanochitosan/YSZ biocomposite is nanometric in nature, the particles are roughly sphere-shaped, and the average size of

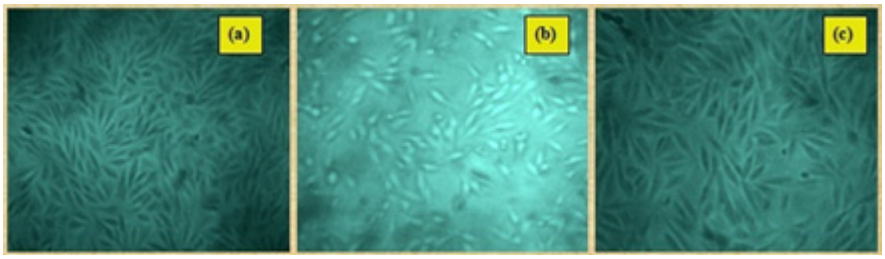

Figure 8: (a),(b) and (c) Microscopic images of Cell for control cell line, uncoated, nano biocomposite coated sample

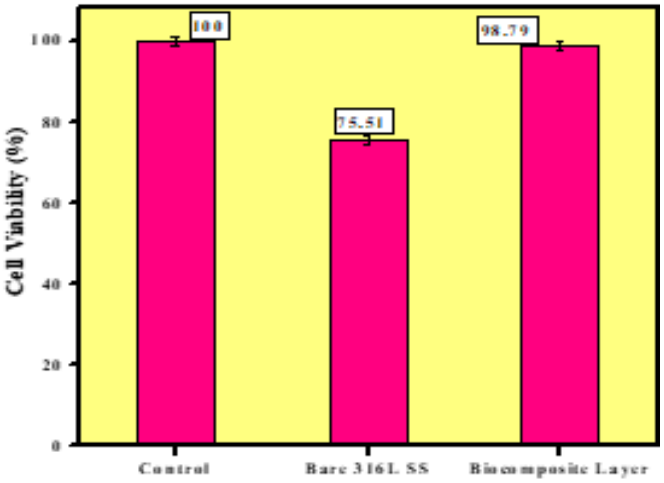

Figure 9: MTT assay results obtained nano biocomposite layer compared with uncoated 316L Stainless steel

nanoYSZ is in the range of 40-80 nm. Raman and FTIR spectra confirmed the formation of nanochitosan/YSZ on 316L stainless steel. The electrochemical studies in artificial saliva revealed that the nanochitosan/YSZ layer exhibited higher corrosion resistance than nanoYSZ and uncoated 316L stainless steel samples. The OCP moved in the nearer direction for the biocomposite layer, and it possessed better polarization resistance and lower capacitance values, as mentioned in EIS measurements. The nanochitosan/YSZ layer might act as a barrier against attack by corrosive ions and also resist penetration of ions from artificial saliva to metal surfaces, which was revealed by electrochemical studies. Hence, the optimized biocomposite-coated 316L stainless steel samples would be a new way to fabricate dental implants.

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