

Corrosion protection of 316L stainless steel by (PVDF/HA) composite coating using a spinning coating technique

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Abstract. Polymer coatings are increasingly used in varied fields and applications from simple coatings of barrier to intricated nanotechnology based composite. In the present study, polyvinylidene fluoride(PVDF)/Hydroxyapatite (HA)coatings were produced by spin coating technique over 316L SS. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to observe the coated 316L SS substrates surface morphology. The corrosion protection efficiency of pure polyvinylidene fluoride and polyvinylidene fluoride/HA nanocomposite coatings on 316L SS was inspected using potentiodynamic polarization along with the ions release techniques in Hank's solution. A superior biocompatibility and an improved protection performance against corrosion were obtained for the 316L SS samples with nanocomposite coatings compared with the pure polyvinylidene fluoride coatings and pristine 316L SS counterparts. The 316L SS samples coated by PVDF/HA nanocomposite showed enhanced corrosion protection within Hank's solution. The corrosion of 316L SS samples within Hank's solution increased from 92.99% to 99.99% when using 3wt% HA due to increasing the PVDF inhibition efficiency. Good agreements in the electrochemical corrosion parameters were obtained from using ions release and potentiodynamic polarization tests.

Key words: 316L SS; polyvinylidene fluoride; hydroxyapatite; Hank's solution; corrosion resistance.

1. Introduction

316L stainless steel (SS) is widely employed in anatomical structure restoration due to its good biocompatibility, high mechanical strength, and cost-effectiveness. This material is frequently used in orthopaedic surgeries, for instance, fracture fixation and replacement of joints [1]. The metallic implantation inside the human body should have an insignificant rate of corrosion. In the last two decades, the corrosion characteristics of metallic implant materials and their ion release have been widely investigated in different physiological situations [2]. Releasing nickel, iron, and chromium from the implant results in a detrimental reaction close to the implanted region that may lead to a permanent failure of the implant. Accordingly, coating and surface modification of the implant is essentially used to resist the prospected corrosion [3]. Polymeric coatings have been widely applied in corrosion inhibition. These coatings act as an obstacle or a protection layer between the metal surface and corrosive species [4].

The stability and cost-effectiveness of polymers as anticorrosive materials have attracted significant interest [5]. Polymers can be efficiently adsorbed on the surface of metals owing to their several adsorption locations (functional groups) displaying a considerable protection behaviour against corrosion. The anti-corrosion behaviour is attributed to the creation of complexes with the surface metal ions that occupy and cover a large sur-

face area and, therefore, protect the metal against harsh solution agents [6, 7].

The spin coating technique is broadly utilized in the production of polymer films. An additional polymer solution is placed on a substrate and is then typically rotated at 1000 to 5000 rpm for dispersing the fluid via the centrifugal force. Later, the solvent evaporation will thin the film. This technique is utilized in developing CDs and in electronic microchips [8]. A very small variation in the coating spin speed or in the solution concentration can cause significant changes in the final thickness. This way, film formation dynamics can be controlled and linked to the film final structure [9].

Pure and extremely unreactive thermoplastic fluoropolymer called polyvinylidene difluoride or polyvinylidene fluoride (PVDF) is formed utilising vinylidene difluoride polymerization [10]. In addition, PVDF can be considered as one of the excellent polymers utilized in manufacturing micro and ultra-filtration membranes because of its good resistance against corrosion and wear, mechanical properties, and film-forming properties and thermal stability as well [11–14].

HA is a bioactive and biocompatible substance that is available in nature and can interact with the surrounding bone [15]. The nanocomposite coatings are efficiently used to protect metals and alloys against corrosion. These coatings can be used as an alternative to poisonous and hazardous compounds. Nanocomposite coating is a solid multiphase substance containing one phase less than 100 nm in size. It works as a protective artificial layer located on the metal surface and repressing the reactions at the anode and cathode electrodes [16, 17].

Due to the importance of polymer-based nanocomposites, the emphasis of this work is on producing PVDF-HA nanocom-

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Manuscript submitted 2020-07-11, revised 2021-02-21, initially accepted for publication 2021-02-23, published in April 2021

posite coatings over 316L SS material utilizing the spin coating technique for implantation of orthopaedic. In particular, this work intends to investigate the potential of using a PVDF-HA nanocomposite coating on 316L SS material to enhance its protective performance against corrosion in the biological field.

2. Materials and methods

2.1. Preparation of 316L SS substrates. A circular 316L SS plate was prepared with a diameter of 12 mm and thickness of 3 mm. The chemical composition of the 316L SS plate was tested in the state-owned Company for Inspection and Engineering Rehabilitation (SIER)/Ministry of Industry and Minerals. Table 1 includes the chemical analysis of 316L SS. All samples were wet grounded utilizing 120, 220, 320, 600, 1000, 1200 and 2000, grit silicon carbide papers. The samples were then cleaned for 10 minutes in the sound cleaning device using distilled water, acetone, and ethanol, respectively.

Table 1
Chemical analysis of 316L SS

Element	Percentage [%]
C	0.023
Si	0.322
Mn	1.00
P	0.038
S	0.00
Cr	17.91
Mo	2.06
Ni	9.85
Al	0.001
Co	0.153
Cu	0.286
V	0.112
Fe	Bal.

The PVDF with a density equal to 1.78 g/cm³ and a particle size of 16 µm, provided by China Guangzhou Li Chang Floro

Plastics Co., Ltd., was used. The characteristics of this polymer were tested by DSC and FTIR. The HA powder with particles having a size equal to 55 nm and purity of 99.9%, supplied by Nanjing Nanotechnology, was used. Dimethylformamide and acetone DMF were used as common solvents for the chemical reaction and were provided by the Central Drug House CDH (P) Ltd. India.

2.2. The coating of the substrate. In the present study, the samples were fabricated in three groups, each one consisting of five specimens, as presented in Table 2.

Table 2
Specimen coding

Description of specimen	Specimen code	Fraction of the polymer PVDF (W%)	Fraction of nanoparticles (W%) HA
Bare 316 L	A	0	0
Pure PVDF	B	100%	0%
PVDF + 1%HA	C	99%	1%
PVDF + 2%HA	C	98%	2%
PVDF + 3%HA	C	97%	3%

The first group included a bare 316L SS specimen, while the second and third groups consist of pure polymer (PVDF) and nanocomposite (PVDF/HA) coatings, respectively.

The PVDF/HA nanocomposite coatings and PVDF polymer coating were fabricated by the spin coating technique (see Fig. 1). The method of preparation included making a pure polymer solution (PVDF) and polymer nano-composite (PVDF/HA) with specific ratios of weight percentage of HA (1, 2, and 3%). The procedure involved PVDF dissolved in 20 ml of DMF and acetone on a certain stirrer tool. The dissolving process was maintained at a temperature of 70°C for 4 hours. The prepared PVDF (polymer nanocomposite) was then dissolved in 10 ml of DMF and acetone on a certain stirrer tool. The dissolving process was maintained at a temperature of 70°C and continued for 4 hours. Then, an ultrasonic mixer was used to mix the nano HA and 10 ml of DMF and acetone at different concentration values of dispersion for 10 minutes only. A glass cylinder containing

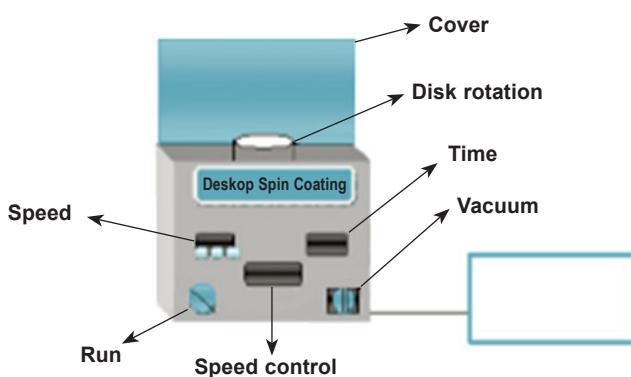


Fig. 1. Schematic and actual experimental spin coating device

2 g of pure polymer was used to prepare the solution. Next, both nano-HA and the polymer solution were added together on the stirrer tool for 2 hours without heat. Then, the prepared samples were spin-coated on the substrate of stainless steel after cleaning it out with acetone under specific coating conditions as shown in Table 3. To reduce the stresses and remove the solvent from the samples, the deposited films were post-annealed at a temperature of 70°C for one hour in a vacuum furnace at a heating rate of 5°C/min.

Table 3
Conditions of spin coating specimens

Description of specimen	Specimen code	Time (min.)	Speed (RPM)
Bare 316 L	A	0	0
Pure PVDF	B	5	10000
PVDF + 1%HA	C1	5	10000
PVDF + 2%HA	C2	5	10000
PVDF + 3%HA	C3	5	10000

2.3. PVDF and PVDF/HA nanocomposite coatings – characterization.

2.3.1. SEM analysis. A scanning electron microscope (TM = 1000 Hitachi tabletop Japan) was used to investigate the surface morphologies of polymer-coated 316L SS.

2.3.2. AFM analysis. The surface topography, depth morphology, and roughness of thin film were analyzed through AFM with an AA3000 Angstrom Advanced Inc. atomic force microscope.

2.4. Electrochemical test.

2.4.1. Solutions. The solution used in this work was Hank's solution (the chemical composition is shown in Table 4) with the pH of Hank's solution equal to 7.4 at 37°C.

Table 4
Chemical composition of Hank's solution [18]

No.	Constituent	(GM./L)
1	NaCl	8
2	CaCl ₂	0.14
3	KCl	0.4
4	NaHCO ₃	0.35
5	Glucose	1
6	Mg Cl ₂ .6H ₂ O	0.1
7	Na ₂ HPO ₄ .2H ₂ O	0.06
8	KH ₂ PO ₄	0.06
9	MgSO ₄ .7H ₂ O	0.06

2.4.2. Potentiodynamic polarization. Electrochemical experiments were performed in a three-electrode cell and electrolytes similar to natural saliva and Hank's solution. The counter elec-

trode was a Pt electrode, and the reference electrode was an SCE and working electrode (specimen) according to the American society for testing and materials (ASTM). The corresponding curves of the potentiodynamic polarization were plotted. Both of the corrosion potential and the corrosion current density (ICorr.) were estimated by Tafel plots by using cathodic and anodic branches. The test was conducted by potential stepping at 0.4 mV/s as a scanning rate from an initial value of the potential of 250 mV below the potential of the open circuit. The scan sustained up to 250 mV above the potential of the open circuit. To measure the efficiency of a PVDF/HA nanocomposite for controlling the dissolution of stainless steel, the efficiency of inhibition (I) was calculated from the polarization curves using Eq. (1) [17]:

$$I\% = \frac{[i_{coor} - i_{coor}(\text{film})]}{i_{coor}} \times 100, \quad (1)$$

where: i_{coor} and i_{coor} (film) are the abbreviations of the values of the corrosion current density measured by (μAcm^{-2}) for bare and coated stainless steel, respectively.

3. Results and discussion

3.1. SEM results. SEM images of the PVDF and PVDF/HA specimen are shown in Fig. 2. The globular structure of PVDF polymer with an average diameter of 1.5 μm is shown in Fig. 2a. The presence of hydroxyapatite with nanoscale in PVDF/HA composite clearly caused a decrease in the diameters of the globular structures and this may be attributed to the role of the nanoparticle that played an important part as a nucleus for the creation of new spherical structures, i.e. the increase in the number of spherical structures at the expense of reducing their diameters. It was confirmed by this observation through continuous decreasing the diameter of the spherical structures with the increased concentration of nanoparticles with 1%, 2%, and 3% weight percentages to 1.25 μm , 500 nm, and 400 nm, respectively (see Figs. 2b, 2c and 2d).

However, it was difficult to recognize the globular structure of the polymeric matrix in the composite with 3% of HA concentration because of the high concentration of hydroxyapatite in the analyzed area. On the other hand, it is important to note that the porous regions between the globes of the coating layer increased with a growing concentration of HA due to the increased viscosity of the nanocomposite coating.

3.2. AFM results. The values of the surface roughness (Ra), root mean square roughness (RRMS), and 3D topography of the polyvinylidene fluoride (PVDF) coatings, for different HA percentages determined by AFM are presented in Fig. 3. As it can be detected, the parameters of the surface roughness varied depending on the introduced amount of HA into the composites at the concentrations of 0.01, 0.02, and 0.03wt. It can be seen that the surface roughness of the resultant films decreased with the increasing percentage of HA in the composite film. The surface roughness (Ra) decreased from 32.5 nm to 17.6 nm

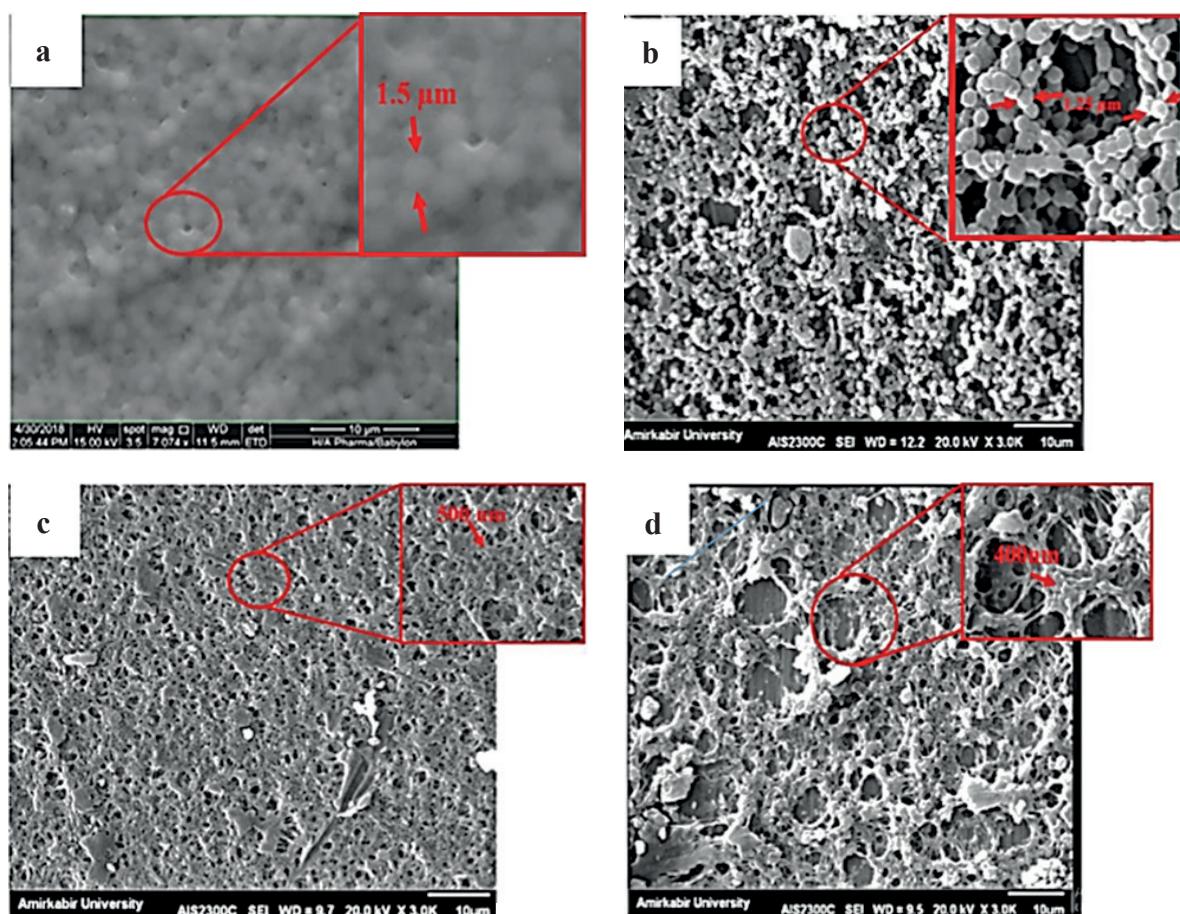


Fig. 2. SEM micrographs of: a) B, b) C1, c) C2 and d) C3 specimen

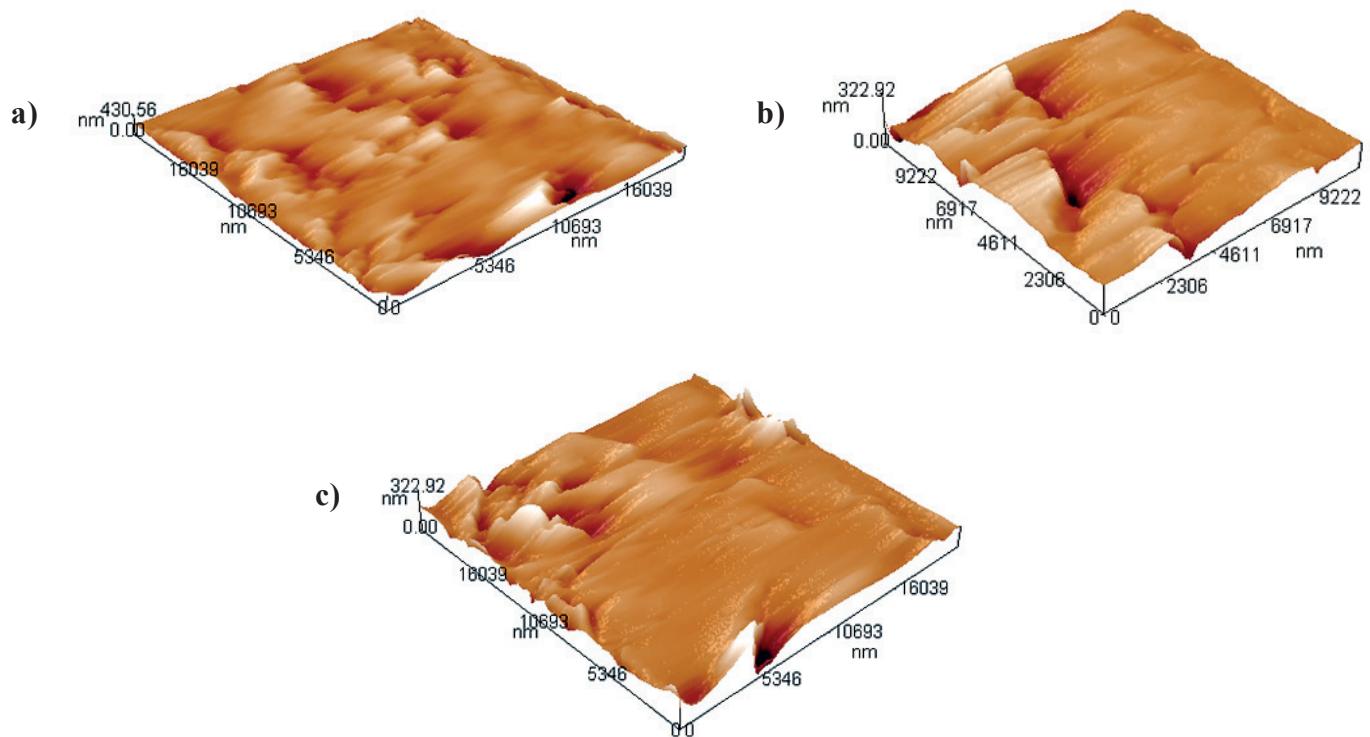


Fig. 3. 3D topography images of coating surfaces conducted by AFM: a) 1%wt. HA, b) 2%wt. HA, c) 3%wt. HA

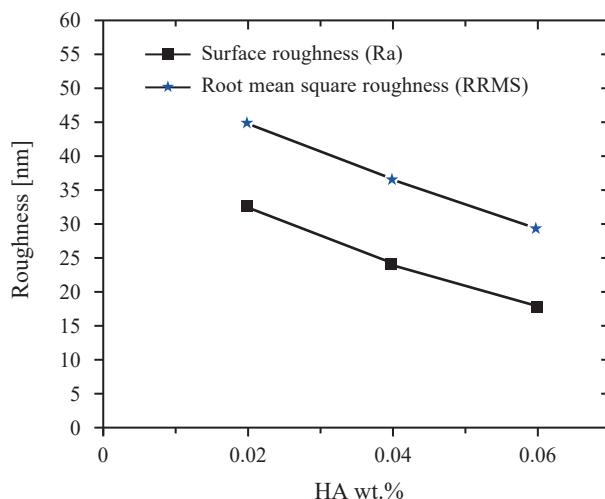


Fig. 4. Surface roughness (Ra) values, root mean square roughness (RRMS) vs HA nanoparticle weight

for 2wt% HA and the root mean square roughness (RRMS) decreased from 44.8 nm for 1wt% HA to 29.2 nm, 3wt% HA (Fig. 4).

3.3. Potentiodynamic polarization test. Potentiodynamic polarization test curves for the uncoated pure PVDF and PVDF/HA coated samples in Hank's solution at 37°C are depicted in Figs. 5–9. The polarization curve of substrates of the coated and uncoated 316L SS are actually dissimilar. It can be detected that there is a noteworthy shift towards the lower current densities for coated samples compared with the uncoated samples. The corrosion current of the PVDF-coated samples are around 11.6×10^{-7} A/Cm² for the B specimen compared with 4.3×10^{-5} A/Cm² for the A specimen as shown in Figs. 5 and 6 and Table 5.

Table 5

The electrochemical parameters calculated using potentiodynamic polarization technique for the corrosion of bare 316L SS, coated with PVDF alone and coated with PVDF/HA nanocomposite in Hank's solution at 37°C

Specimen code	E _{corr} mv	I _{corr} A/cm ²	β_c mV/Dec ⁻¹	β_a mV/Dec ⁻¹	I %
A	-717.8	4.35×10^{-6}	-45.9	10.8	
B	-114.3	11.6×10^{-7}	-39.4	36.1	79
C1	-189.5	9.81×10^{-7}	-66.6	67.8	82
C2	-36	2.64×10^{-7}	-30.7	142	96
C3	-185.4	1.26×10^{-7}	-94.3	86	98

These results confirm our earlier assumption that PVDF coating significantly reduces metal ion release for 316L SS substrate and decreases the corrosion rate of these alloys in a biological solution [18], which means that the obtained pure PVDF coating was uniform and compact and its adhesion to the substrate was very good. An overall protective PVDF surface

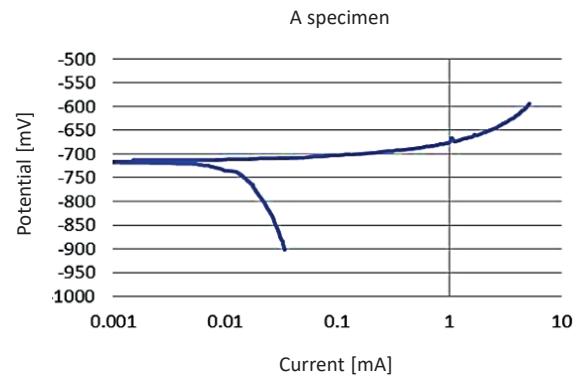


Fig. 5. Potentiodynamic polarization curves obtained for the A specimen in Hank's solution at 37°C

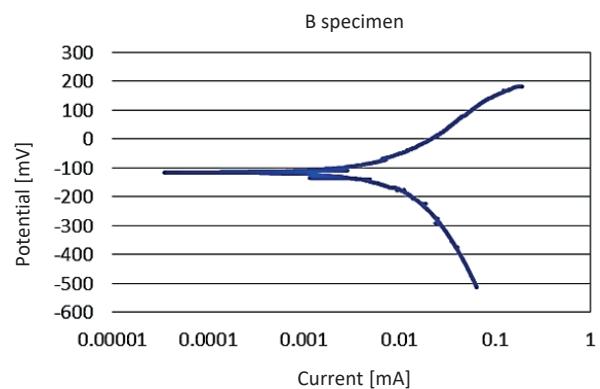


Fig. 6. Potentiodynamic polarization curves obtained for the B specimen in Hank's solution at 37°C

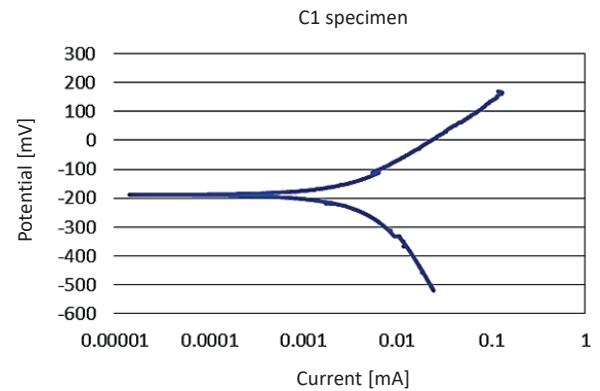


Fig. 7. Potentiodynamic polarization curves obtained for the C1 specimen in Hank's solution at 37°C

layer may ensure outstanding corrosion resistance and biocompatibility. These findings are in agreement with other studies which indicate that coating stainless steel with a polymeric barrier does in fact improve corrosion resistance [19].

It should also be pointed out that the corrosion potential of an uncoated sample is just slightly higher as compared to that of the PVDF coated one.

A significant reduction was noted in the current required for the dissolution for the nanocomposite-coated specimen as com-

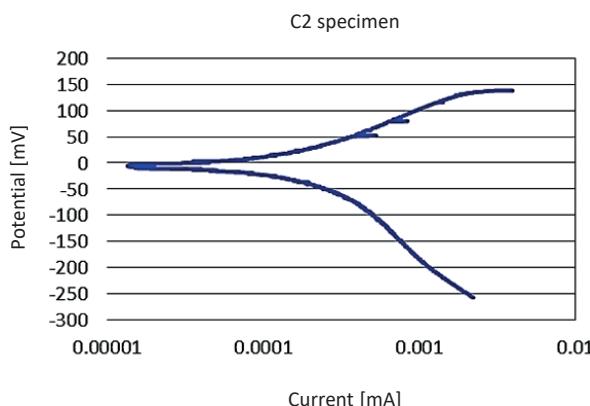


Fig. 8. Potentiodynamic polarization curves obtained for C2 specimen in Hank's solution at 37°C

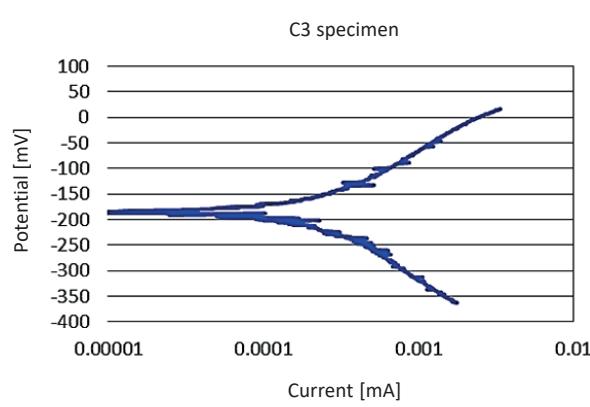


Fig. 9. Potentiodynamic polarization curves obtained for C3 specimen in Hank's solution at 37°C

pared to the bare stainless steel and pure polymer-coated specimen after inspecting the value of the current density exactly at the same polarized potentials.

From Figs. 5 and 7, it is easy to note that for bare stainless steel corrosion, the current density increased as the voltage increased. That increment happened rapidly up to $4.35 \times 10^{-6} \text{ A/cm}^2$. The presence of the PVDF/1% HA nanocomposite coating increases the corrosion resistance by decreasing the current density from $4.35 \times 10^{-6} \text{ A/cm}^2$ for the A specimen to $9.81 \times 10^{-7} \text{ A/cm}^2$ for the C1 specimen. The reduction in anodic current density became more significant when using PVDF/2% HA nanocomposite coating (Fig. 8), where it reached a value of $2.64 \times 10^{-7} \text{ A/cm}^2$ for the C2 specimen. Moreover, as can be seen in Fig. 9, the nanocomposite coating of PVDF/3% HA had a more distinct effect on the value of the corrosion current ($1.26 \times 10^{-7} \text{ A/cm}^2$) for the C3 specimen and, henceforth, the corrosion rate led to an increase in the inhibition efficiency to 98 for the C3 specimen, while the inhibition efficiency for the C1 and C2 specimens reached 82 and 96, respectively, as shown in Table 5.

Barrier coating usage is essential to suppress the corrosion in a biological solution by controlling the diffusion of harmful ions, and electrons to the metal surface. Furthermore, the coating reduces the hydrolysis water content and leads to a signifi-

cant decrease in the corrosion current values in the anodic curves, which provides a high level of noticeable corrosion protection. The coated film works as a strong and efficient passivation layer for the diffusion of ions and corrosion [20].

The implant material coated with polymer/ceramic composite attracted more attention to achieve the combination of bioactivity and biocompatibility properties, which cannot be achieved by coating them with polymer or ceramic alone [21]. Also, studies indicated that the composite HA/polymer coating for the surface of the metallic implant proved to have a more corrosion-resistant and more favourable surface for getting a bone marrow cell attachment than an unincorporated polymer coating because HA is known to be an osteon-inductive material [18, 22].

3.4. Ni release results. The ions of nickel that released sufficient quantities from nickel-containing alloys, can cause allergic contact dermatitis or nickel sensitization. In order to ensure the 316L SS capability before and after the coating is used in human bodies, Ni ions release test is used. Figure 10 illustrates the Ni ions concentration for the uncoated and coated specimen after 5 weeks of immersion in Hank's solution maintained at 37°C as shown in Table 6. From the figure and the table, it is obvious that the measurable amounts 8.567 ppm of Ni ions are released from the uncoated specimen, while the measurable amounts for the coated sample with pure PDVF are 0.413 ppm. These quantities are much lower than the uncoated specimen.

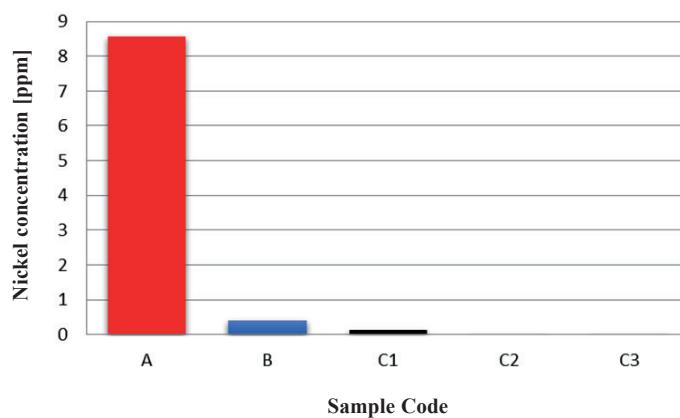


Fig. 10. Nickel ion concentration values for the coated and uncoated specimen in Hank's solution at 37°C for 5 weeks

Table 6
AAS data corresponding to Ni concentration released from the coated and uncoated specimen in Hank's solution at 37°C for 5 weeks

Specimen code	Ni concentration (ppm)
A	8.567
B	0.413
C1	0.119
C2	ND
C3	ND

These results show that polymer coating reduces the release of Ni ions from 316L SS alloy.

The reduction in Ni-ion release becomes more substantial when using PVDF/1% HA nanocomposite coating, with a value of 0.119 ppm for the C1 specimen. Moreover, the release of Ni ions from the C2 and C3 specimens, which represent PVDF/2% HA and PVDF/3% HA nanocomposite coating, respectively, was not detected in Hank's solution at 37°C, as presented in Fig. 10 and Table 6.

These results confirm our earlier assumption that a pure PVDF coating and nanocomposite PVDF/HA coating significantly reduce metal ions release from 316 SS alloy by forming a protective and strongly adherent coating layer on the surface of alloy which limits the release of Ni ions. These results agree with those of other researchers [23].

4. Conclusion

The PVDF/HA nanocomposite coating on 316L SS substrates was prepared by the technique of spin coating. HA nanoparticle presence in a PVDF matrix was ensured by SEM and AFM analyses. The electrochemical work discovered that HA nanoparticle presence in a PVDF matrix improved the performance of the corrosion protection of the coated 316L SS substrates in Hank's solution. The presence of 3 wt% HA increases the efficiency of inhibition of PVDF against stainless steel corrosion in Hank's solution from 92.99% to 99.99%. According to the previous findings, the PVDF/HA nanocomposite coating (which was considered as the prospective candidate coating material for 316L SS bioimplants) has better biocompatibility and enhanced corrosion resistance.

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