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In-vitro corrosion response of hydroxyapatite/halloysite nanotube/bismuth reinforced poly– (lactic acid) hybrid coatings on biodegradable magnesium

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Abstract

Magnesium (Mg) and its alloys have attracted a lot of attention as possible biomedical materials because of their mechanical characteristics that mimic those of real bone, particularly their low Young's modulus and biocompatibility. However, their long-term stability is challenged by the intrinsic sensitivity of magnesium to corrosion in physiological environments. Because of this, researchers are developing smart multifunctional coatings for magnesium biomedical materials that incorporate hydroxyapatite (HA), which has a structure akin to that of human bone, in a synergistic manner. Still being researched, though, are more elements that will show specific features in along with HA. This study offers a viable method for integrating HA, Halloysite nanotubes (HNT), and bismuth (Bi) into a poly– (lactic acid) (PLA) matrix to modify the surface characteristics of magnesium biomedical materials. Two important factors were taken into consideration when designing the coatings: improving biocompatibility and offering corrosion resistance. A bioactive ceramic called HA facilitates osseointegration, while hybrid nanotubes (HNT) provide a special nanostructure for regulated drug release and enhanced mechanical characteristics. Bi, which is well-known for its ability to prevent corrosion, strengthens the coating even more against deterioration in physiological environments. The hybrid coatings are applied to the magnesium substrate using the spin-coating technique after HA, HNTs, and Bi are dispersed within a PLA matrix. The coatings were characterized for surface morphology with a scanning electron microscopy (SEM). In-vitro corrosion features were revealed with using open circuit potential (OCP), potentiodynamic polarization spectroscopy (PDS), and electrochemical impedance spectroscopy (EIS) methods, respectively. Results indicate that the developed coatings exhibit, leading to enhanced corrosion resistance of the Mg substrate due to the reinforcements (HA, HNTs, and Bi) (I_{corr} values). The multifunctional coatings pave up the opportunity to the production of cutting-edge, biocompatible materials for orthopaedic and implant applications and provide an exhaustive solution to the problems posed by magnesium corrosion. I_{corr} values was calculated as 13215.00×10^{-9}, $A \cdot cm^{-2}$, 885.25×10^{-9}, $A \cdot cm^{-2}$, 302.10×10^{-9}, $A \cdot cm^{-2}$, and 6.15×10^{-9}, $A \cdot cm^{-2}$ was calculated for uncoated Mg, PLA/HA-HNT, PLA/HA-HNT-Bi1, and PLA/HA-HNT-Bi3 coated Mg specimens, respectively. On the other hand, an increasing radius with the addition of Bi was observed in the EIS results, which was interpreted as a result of the increased resistance of the coatings to oxidation.

Keywords: In-vitro corrosion; Hydroxyapatite; Halloysite nanotube; Bismuth; Poly- (lactic acid) coating.

1. Introduction

Biodegradable magnesium alloys are frequently preferred in biomedical implant applications due to their mechanical properties, biocompatibility and biodegradability. These alloys provide optimum load transfer during the healing process after implantation because their mechanical properties are similar to natural bone. One of its most important advantages is that the biomaterial gradually dissolves in the body without the need for removal from the patient's body, that is, without the need for a second operation. Moreover, due to this feature, risks such as inflammation and infection associated with long-term implant presence are minimized [1]. Although these alloys are often preferred due to their advantages, the instability of mechanical rigidity during the healing process and the uncertainties of potential inflammatory responses caused by rapid dissolution must

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be prevented. Research conducted in recent years is aimed at eliminating these possible risks by controlling the existence of this rapid biodegradation. Researchers are conducting studies on surface modifications with hydroxyapatite and biodegradable polymer materials in order to slow down the rapid biodegradation of Mg and its alloys and increase their biocompatibility [2].

Poly- (lactic acid) (PLA) coatings applied on Mg alloys are expected to serve two different purposes. The first of these is that PLA protects Mg surfaces from aggressive physiological environments and acts as a barrier. Therefore, the sensitivity of Mg to rapid dissolution can be reduced and a more controlled ion release and corrosion behavior is achieved. The second can be summarized as creating a more compatible layer between the environment and Mg due to the lactic acid released into the environment by PLA during the dissolution process [3]. Thanks to this dual feature, the implant candidate can reduce the risk of complications in long-term use without a secondary surgery. For this reason, researchers are carrying out studies to increase the performance and functionality of Mg surfaces with various surface modification techniques. The most popular of these today are composite surface coatings reinforced with different PLA-based filling materials. Hydroxyapatite (HA) reinforcements, which have an elemental composition similar to bone, are frequently preferred in these coatings [4]. HA reinforced PLA coatings represent a compelling strategy in the development of advanced biomaterials for biomaterials. Naturally occurring mineral form of Ca-P, HA is widely recognized for its similarity to the inorganic component of human bone [5]. When incorporated into PLA coatings, HA shows unique properties that enhance the overall performance and biocompatibility of the Mg alloys. Key aspects of HA-reinforced PLA coatings are, (i) osteoconductivity and bioactivity: bone mimicry, and bioactivity, (ii) mechanical enhancement: improved strength, and reduced brittleness, (iii) biocompatibility: tissue Integration, and reduced Inflammatory response, (iv) controlled degradation, and (v) therapeutic potential [6]. The main purpose of using PLA-HA composite coatings is to increase its biocompatibility with surrounding tissues in addition to providing the insufficient mechanical rigidity that PLA has due to HA reinforcement. However, scientists are still carrying out different studies to produce coatings that may exhibit different properties other than HA. Some of these are Halloysite nanotubes (HNT) and Bismuth (Bi) [7].

HNT minerals are essentially wrapped tube-type forms of naturally occurring kaolinite minerals. These nanotubes exhibit a high aspect ratio and are characterized by their internal and external properties. HNTs have high biocompatibility and are widely used in various biomedical applications. Due to their shape, they are frequently used in effective encapsulation of therapeutic agents and controlled release applications, that is, drug release systems. Moreover, they serve as carriers in the use of growth factors in tissue engineering and play a role in supporting cell proliferation [8]. As a result of scientists' research on the use of Bi element as a biomaterial, with its low toxicity and radiopaque properties, even though it is known as a heavy element, Bi element is used to increase visibility in x-ray and computed tomography (CT) scans. On the other hand, Bi has unknown antimicrobial properties and the potential to treat infections. As a result of the simultaneous use of HNT and Bi, the unique properties of both materials can be advantageous in various applications ranging from drug delivery and medical imaging techniques to therapeutics [9,10].

For various reasons, many methods are used in the surface modification of implant candidates, and sometimes even the development of hybrid methods can be observed. Some common techniques include electrochemical deposition, sol–gel processes, physical vapor deposition, and spin coating [11]. Among these, the spin-coating method can be frequently preferred in drug delivery systems and implant coatings. In the method where the thickness of the coatings can be controlled due to the number of cycles, different thicknesses can be obtained in a single layer depending on the viscosity of the solution. In addition to other methods, the method can be preferred because it has simplicity, versatility and efficiency. Moreover, during the synthesis of polymer structures such as PLA on the implant candidate, it can help remove alcohol-based components in the structure due to rotation. Due to these advantages, the spin-coating method is frequently preferred in surface modification processes of various biomaterials [12].

In the previous study, the effect of HNT on PLA-HA based coatings on Ti-6Al-4V surfaces was compared with the dip-coating method [13]. From the results obtained, it was observed that the crystallinity of the coatings increased with HNT reinforcement and furthermore them in-vitro corrosion behavior improved. The difference of this study can be presented as both the choice of the spin-coating method and the investigation of whether the in-vitro corrosion resistance of the coatings can be further increased with the addition of Bi. In brief, different amounts of Bi element additives were investigated to increase the corrosion resistance in previously applied HA

and/or HNT reinforced PLA coatings. It has been investigated in detail how the Bi reinforcement changes the morphology of the surface and effect it has on the in-vitro electrochemical corrosion behavior.

2. Material and Method

In the study, 10×10×1 mm sized biomedical grade Mg plates were used as the substrate material, and PLA, HA, HNT, and Bi were used as coating agents, respectively. Before the coating process, Mg surfaces were sandblasted in order to obtain higher adhesion strength at the interface [1]. Al_2O_3 powders (250 μm) was used as sand, and process was applied to each sample for 15 s under 8 bar pressure. In line with the literature, the dissolution rate of PLA in chloroform was chosen as 1/10 (g/ml) [13]. While PLA/chloroform ratio remained constant, HA, HNT and Bi additives calculated according to different compositions were used (0.5 g for both HA and HNT, but 0.1 g and 0.3 g Bi reinforcement for PLA/HA-HNT-Bi1 and PLA/HA-HNT-Bi3 composition). More clearly, the use of the following abbreviations for PLA/HA-HNT, and PLA/HA-HNT-Bi coatings will increase understanding; HH, HH-Bi1, and HH-Bi3. The coatings were carried out in two stages using the spin-coating method. In the first stage, the PLA-based solution was held on the surface at low speed (500 rpm for 5 s), followed by high speed (6000 rpm for 10 s) to cover the entire surface. The speed and time parameters used during spin-coating were optimized by trial and error during preliminary studies. Although tests were not carried out on the adhesion behavior of the coatings within the scope of the study, since it is known that the adhesion resistance of thin film coatings on the surfaces is high, the thickness of the coatings was tried to be controlled with three drops of approximately 1 ml from the syringe tip for each coating. Since the surface morphologies of the coatings on Mg substrates indirectly affect the in-vitro corrosion properties, they were tried to be revealed using scanning electron microscopy (SEM: device information). Then, simulated body fluid (SBF: Kokubo's solution) was used to reveal the electrochemical behavior of the coatings under in-vitro conditions. Kokubo's solution consists of the following elements, respectively (16 g NaCl, 800 mg KCl, 280 mg $NaCl_2$, 200 mg $MgSO_4{\cdot}7H_2O$, 200 mg $MgCl_2{\cdot}6H_2O$, 120 mg $Na_2HPO_4{\cdot}2H_2O$, 120 mg KH_2PO_4, 2 g D-glucose, and 700 mg $NaHCO_3$ used for prepare 2000 mL SBF.) was prepared in accordance with the specified recipe. To reveal the in-vitro electrochemical corrosion behavior of the coatings, the three-electrode method was preferred and platinum wire, Ag/AgCl and coatings were used as the counter electrode, reference electrode and working electrode, respectively. In-vitro electrochemical corrosion behaviors were tried to be determined by open circuit potential (OCP), potentiodynamic polarization spectroscopy (PDS), and electrochemical impedance spectroscopy (EIS) measurements, respectively.

Using the Stern and Geary equation (Eq. 1), the corrosion current density (I_{corr}) value and polarization resistance (R_p), two crucial corrosion resistance characteristics in electrochemical corrosion measurement tests, were determined.

$$I_{corr} = \frac{\beta_\alpha \times \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} \quad (1)$$

From PDS curves, β_a, β_c, and R_p represented the anodic and cathodic branch Tafel slopes, and polarization resistance, respectively. The general synthesis and production process of the coatings is presented in the flow-chart Figure 1.

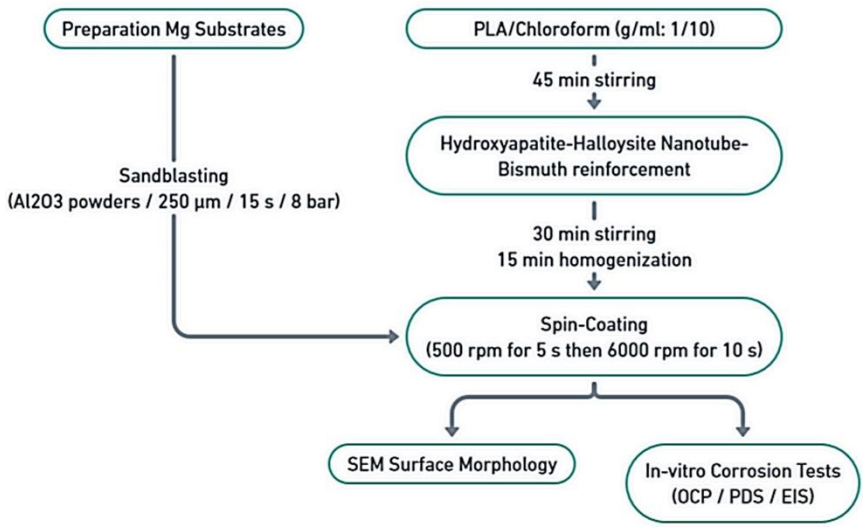

Fig. 1 Flow-chart of synthesis of coatings

3. Results and Discussion

SEM surface morphologies of the coatings before electrochemical corrosion tests are presented in Figure 2. After sandblasting, the surfaces have a characteristic indented-protruding morphology and it was predicted that the penetration of the coating would improve (Figure 2a). In other words, it is thought that such surfaces can serve as anchorage between the coating and the base material. As a result, it is thought that it may prevent the formation of filiform corrosion, especially under in-vitro conditions. It has been revealed that structures similar to the films previously obtained spontaneously by the spin-coating method have similar morphologies in each coating produced [14]. It has been stated that such surface morphologies obtained are due to both the solvent used to dissolve PLA and the humidity in the environment. In the surface morphologies presented in Figure 2b-d, in addition to the presence of these micropores on the surfaces, the presence of other materials (HA, HNT, and Bi) filled into PLA is also seen in the inner parts of the pores. Moreover, it is frequently stated by researchers that such surfaces can play an active role during possible biomaterial - tissue interaction [15]. However, this may be considered an undesirable situation in coatings on Mg, which is a biodegradable material. From the SEM surface morphologies, it is clearly seen that the coating composition affects the micropore size and distribution on the surface (Figure 2b-d). It was observed that with the addition of Bi into HA-HNT, the pore size initially increased but decreased with increasing Bi. Porous area per counts along with the surface was also calculated and presented in Figure 3. Both SEM surface morphology and surface porosity fraction well matched with each other. It is thought that this may be due to the effect of Bi on the amount of chloroform evaporating from the surface. Both the moisture capacity of the coatings and the density of PLA may change with changing amounts of reinforcement [14].

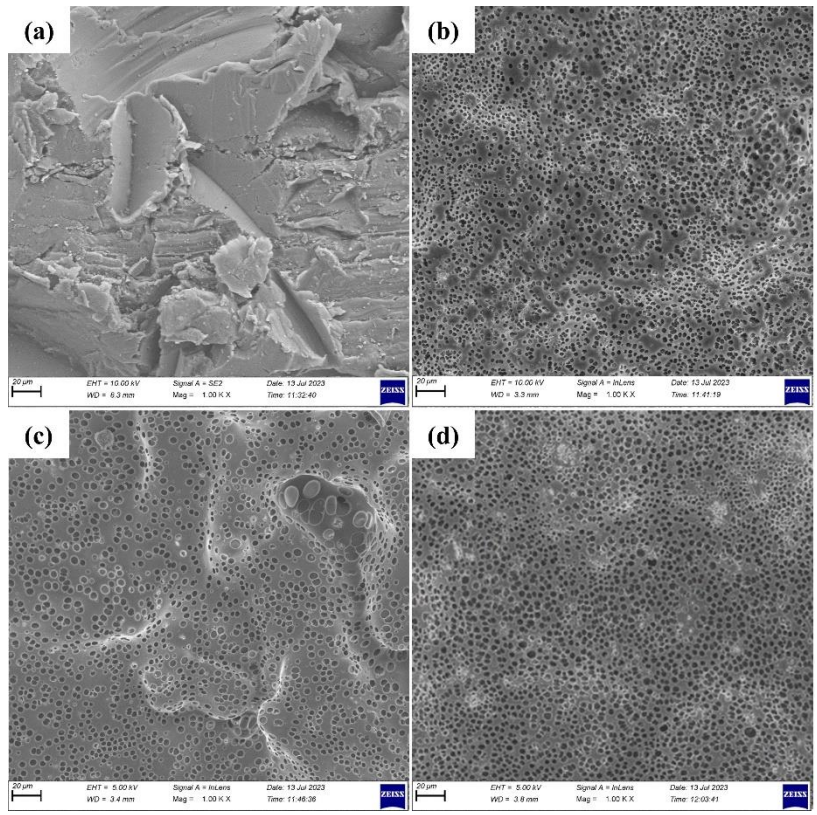

Fig. 2 SEM surface morphology of (a) uncoated, (b) HH coated, (c) HH-Bi1, and (d) HH-Bi3 coated samples

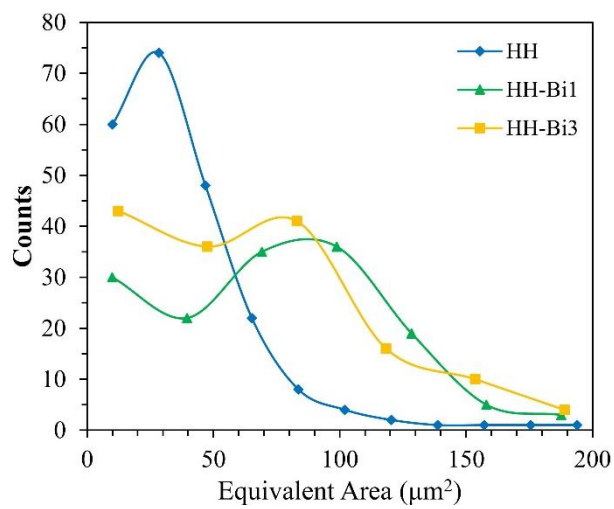

Fig. 3 Surface porosity area fractions for coatings

While micropores on the surface improve bio-anchorage, on the other hand, they have the potential to accelerate the dissolution time of Mg. Therefore, if the coatings applied on Mg are porous, the electrochemical corrosion properties under in-vitro conditions must be thoroughly examined. For this reason, the in-vitro electrochemical corrosion test results are presented in Figure 4. From the OCP test results presented in Figure 4a, it can be seen that each coating showed a stable potential behavior at approximately 1800 s. As presented in Figure 4a, time-dependent potential fluctuation was observed in all samples. It is thought that the indented - protruding morphologies seen from the surface morphologies explain the potential fluctuation along the surface

(Figure 2). As a matter of fact, in these pit-like low profile plateaus, the solution remains more stable and while the potential remains constant, changes are observed in the potential values due to the concentration difference with increasing time. On the other hand, when the potential (E) - current density (I_{corr}) graphs of the samples under forced current are examined, as presented in Figure 4b, it is seen that the HH-Bi3 sample has the noblest potential behavior, followed by HH-Bi1, HH, and uncoated samples, respectively. However, it has been stated by many researchers that the corrosion in potential values alone will not be sufficient in terms of electrochemical corrosion resistance, and therefore a comparison should be made based on the corrosion current density (I_{corr}) values on the surfaces of the samples [16]. These values calculated with the Tafel extrapolation method are presented in Table 1. It has been concluded that obtaining such low corrosion currents is undoubtedly a result of the high corrosion resistance feature of the Bi element [17]. However, the fact that there is not much difference in I_{corr} values between 0.1 g and 0.3 g Bi reinforcement may be due to possible agglomeration in the coating, rapid removal of PLA from the coating, and the difference in coating thicknesses (41 ± 07, 47 ± 11, and 52 ± 08 µm for HH, HH-Bi1, and HH-Bi3 coatings, respectively). Moreover, it is thought that it may be due to the effect of the distribution and size of the pores observed in the surface morphologies.

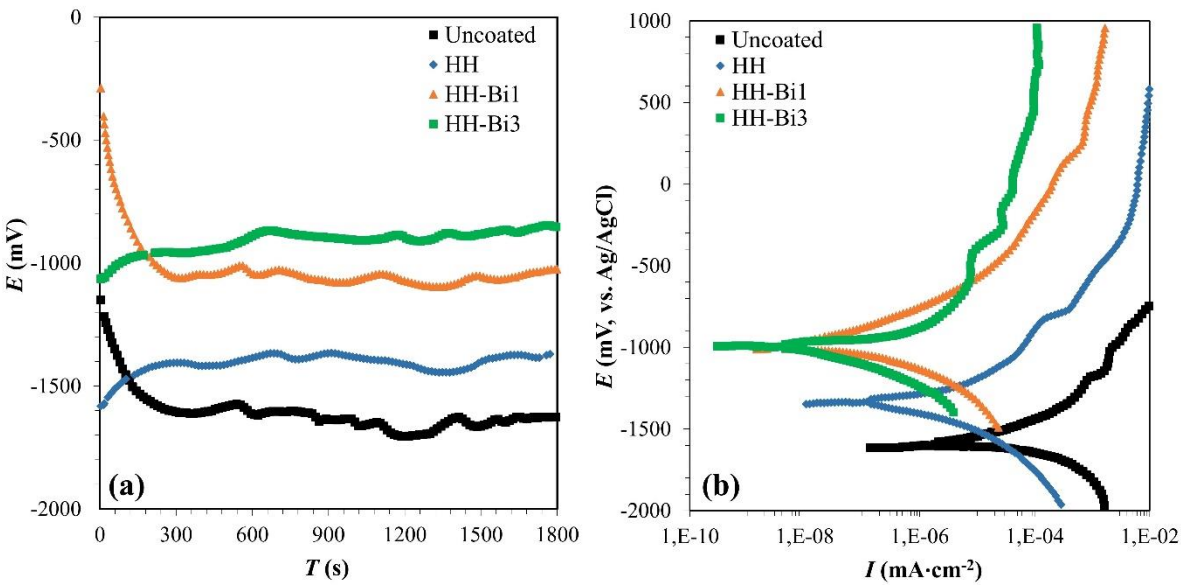

Fig. 4 In-vitro electrochemical curves of samples; (a) OCP and (b) PDS

Table 1. Electrochemical corrosion parameters from PDS curves by Tafel extrapolation method

Sample	E_{corr} (mV)	I_{corr} (x10^{-9}, A·cm^{-2})	β_a (V/decade)	β_c (V/decade)	R_p (Ω·cm^{-2})
Uncoated Mg	-1613.40	13215.00	742.16	213.00	5.44E+03
HH coated	-1347.48	885.25	5426.93	2925.28	9.32E+05
HH-Bi1 coated	-996.42	302.10	38621.41	26799.57	2.27E+07
HH-Bi3 coated	-994.13	6.15	63876.08	84718.40	2.57E+09

In Figure 5, the EIS test results (Nyquist plots) performed to examine the characterization of the oxide films formed on the surfaces of the coatings are presented. From the EIS results, at first glance, a two-stage radius formation stands out. The first conclusion to be drawn here is the radius of the first circle in the Nyquist curves and indicates the resistance of the surface oxide films of the coatings [13]. Accordingly, the stability of the surface oxide films of the coatings of HH-Bi3, HH-Bi1, HH, and uncoated samples, respectively, is seen to be high. Moreover, it is predicted that such two-stage curves may belong to the mixed control circuit model with the Warburg element [17,18]. In short, there is a simultaneous effect of both kinetic and diffusion processes on surfaces. Moreover, it is clearly seen in the EIS graphs when compared to the PDS curves, and it has been

revealed that the HH-Bi3 coating is more electrochemically resistant under in-vitro conditions. Due to the presence of Bi particles near the surface, the existence of a double-layer oxide film can be mentioned. Moreover, different Nyquist curves can be obtained due to the presence of different elements in the interior of the pores on the surface, the distribution of the pores, and their size. In future studies, it will be tried to determine which electrical circuit model the fitting coatings have, based on the data obtained from Nyquist curves.

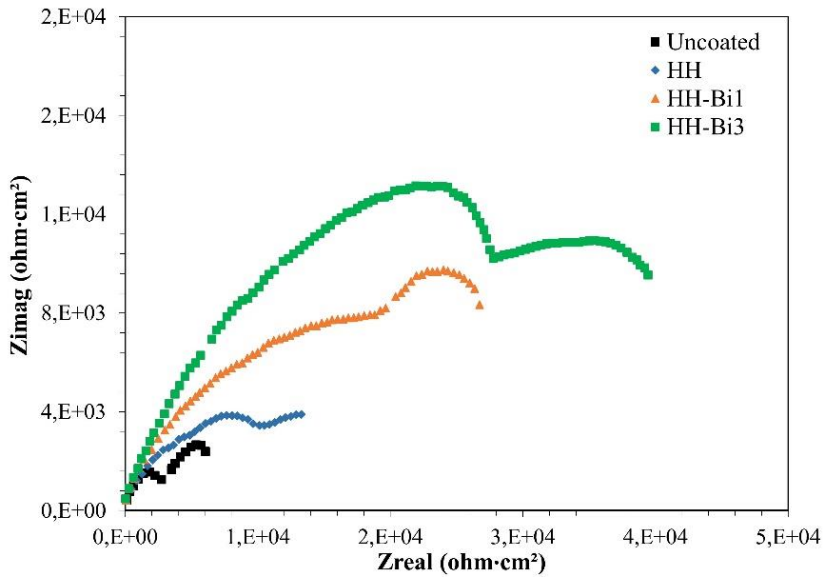

Fig. 5 Electrochemical impedance spectroscopy (EIS) of samples

4. Conclusion

In the study, the in-vitro electrochemical behavior of PLA-based Hydroxyapatite-Halloysite nanotubes-Bismuth reinforced hybrid coatings, which can increase the use of Magnesium as a medium – long term implant material, was examined. In this regard, SEM examinations were carried out to reveal the surface morphologies before in-vitro electrochemical corrosion tests. As a result of the study, it was observed that the surfaces had a very indented profile after the sandblasting process, and there were pores of different sizes and numbers on the surface along with the coatings applied. It has been proven as a result of literature and experiments that the porous surfaces obtained after coating are obtained due to the removal of chloroform used to dissolve PLA, and moreover, the size of these pores can be controlled by ambient humidity. As a result of in-vitro electrochemical tests, it was observed that the I_{corr} values of the coatings decreased with the Bi additive, meaning the corrosion resistance increased. It was concluded that this may be due to the surface morphology or the agglomeration of the Bi reinforcement in the coating. From the Nyquist curves obtained as a result of EIS tests, it was observed that the stability of the oxide films formed on the surfaces of the coatings increased with Bi reinforcement and the formation of a double-layer oxide film. It was concluded that all obtained in-vitro electrochemical corrosion behaviors were related to surface morphologies, especially after surface modification. In short, surface characteristics and electrochemical behaviors must be considered together, especially in biodegradable biomaterials such as Mg.

Author Contribution Statement

Mehmet Topuz confirms sole responsibility for study conception and design, data collection, analysis and interpretation of results, and manuscript preparation.

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