Effect of PMMA sealing treatment on the corrosion behavior of plasma electrolytic oxidized titanium dental implants in fluoride-containing saliva solution

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Abstract
Titanium (Ti) and its alloys are widely used as dental implant materials because of their high mechanical properties, biocompatibility, and corrosion resistance. This research was undertaken to study the effect of polymethyl-methacrylate (PMMA) sealing layer on the corrosion performance of plasma electrolytic oxidation (PEO)-coated titanium-based dental implants in pure saliva and fluoride-containing saliva solutions. The phase structure, chemical composition, and microstructure of coatings were investigated via x-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy, respectively. The corrosion behavior of the samples was evaluated by open circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy tests. The deposition of the PMMA layer on the PEO-coated Ti dental implants was found to effectively seal the micropores and microcracks of the TiO₂ coatings and block corrosive ions’ penetration routes through the coating. Thereby, the results indicated that better corrosion performance was observed when the PMMA layer is applied on PEO-coated Ti dental implants than on the simple PEO coatings.

1. Introduction
The replacement of a lost tooth has been exasperated by biomaterials. A variety of metallic, ceramic and polymeric biomaterials have been used in the dental transplant [1–3]. Titanium (Ti) and its alloys are suitable materials for manufacturing orthopedic and dental implants, due to their high mechanical strength, corrosion resistance, and biocompatibility, which are the reasons for their popularity [4, 5]. A thin oxide layer of titanium dioxide (TiO₂) forms on Ti surfaces exposed to water or air, providing corrosion resistance [6]. Since body environmental conditions can affect the nature, composition, and thickness of the protective oxide layer on metallic surfaces, Ti and its alloys alloy are not considered entirely inert in the physiochemical media [7, 8].
Recent studies have shown that saliva, fluorides, acid attack, \( \text{H}_2\text{O}_2 \), microbial components, bacterial metabolites, and nicotine, adversely affect Ti’s electrochemical behavior [9–11].

The oral environment is often characterized by aggressive properties and corrosive substances [12, 13]. Saliva is complex solution and consists of both inorganic salts and organic compounds [14]. The pH of saliva around dental implants can vary depending on factors such as food, age, and diseases [15]. Drinking acidic beverages can lower buccal pH [16]. Saliva can also be acidified by infections, causing dental implants to corrode [17]. Moreover, fluoride containing toothpaste, prophylactic agents, dental rinses, and other prophylactic treatments are frequently used in dentistry to prevent plaque formation and caries [10]. There is a wide variety of fluoride ion concentrations in these products, ranging from 1 to about 22000 ppm, depending on which therapies and agents are used [18]. Therefore, the corrosion resistance of metallic dental devices must be high at high levels of fluoride ion [19, 20]. Historically, corrosion of titanium-based alloys in fluoride-containing media has been a problem [21, 22].

Up to now, Ti implant surfaces have been modified using topographical, chemical, and biological treatments to enhance their corrosion resistance and bioactivity in physiochemical media [23, 24]. Among the various treatments, plasma electrolytic oxidation (PEO) is one that can be applied to valuable and non-valuable metals [25–28]. The PEO process is a promising method for improving corrosion and bioactivity properties of Ti and its alloys, as a result of the formation of thick, dense and hard oxide coatings [29]. During this process, the Ti sample is anodized above its dielectric breakdown potential in order to break down the TiO_2 coating [30]. There are many benefits to using TiO_2 as surface coatings on dental implants, including its biocompatibility, corrosion resistance, antimicrobial properties, and nontoxicity [31]. It has been reported that TiO_2 formed on titanium becomes extremely reactive when exposed to fluoride ions [32]. However, in light of the literature, no study has been done on the corrosion behavior of TiO_2 coatings produced by PEO method on Ti in fluoride-containing saliva solution.

Due to electrical discharge during the anodic oxidation process, PEO coatings have a porous structure. These pores can be served as pathways for the diffusion of aggressive agents such as \( \text{Cl}^- \) ions through coatings to the substrate, resulting in decreased corrosion resistance [33–35]. In response to this issue, the pores can be sealed by organic or inorganic particles [36]. These particles promote the bone growth on the implant surface by increasing the cell activity [37, 38]. Moreover, sealing pores was introduced as a practical strategy by epoxy deposition technology on PEO coatings [39]. A number of interesting benefits of sealing technology are not only its ability to penetrate deeply into PEO coating pores, but also its ease of manufacturing or its low environmental impact [40, 41]. Moreover, filling the pores of the PEO coating with polymer as a top coat will result in higher corrosion performance in aggressive media [39, 42]. There have been a number of studies using the polymeric sealing strategy for modifying the corrosion performance of PEO coated metallic materials [40, 43]. In such systems, the barrier properties of the epoxy sealing layers determine the system’s performance, preventing corrosive electrolytes and ions from accessing substrates [44]. Epoxy coatings containing inorganics are more prone to cracking since residual water evaporates rapidly during curing [45, 46]. Therefore, in recent years, much attention has been paid to organic layers for sealing PEO coatings. Poly(methyl-methacrylate) (PMMA) is one of the most commonly used organic compounds for total hip prosthesis fixation because it is biocompatible, processable, and inexpensive [47, 48]. With non-toxic solvents, PMMA can be synthesized into a durable, scratch-resistant, transparent thermoplastic that is FDA-approved, biocompatible, bioinert and durable [32]. In addition to providing a strong mechanical connection with the implants, this polymer can also distribute their load when applied as bone cement [49, 50]. Recently, Schott et al. grafted and spin coated PMMA on the alkali activated Ti [51]. They reported the corrosion resistance of the PMMA-grafted/Ti interface in biological medium is satisfactory and that the grafting of PMMA is even acting as a protective barrier for Ti substrate. To the best of our knowledge, this type of polymer has never been deposited on PEO-treated Ti implants to produce duplex PMMA/TiO_2 coatings, and its corrosion behavior has not been reported in an oral environment.

Taking into account the current research directions in the field of surface engineering of dental implants, and the requirements for modifying the corrosion performance of PEO coatings on Ti-based dental implants, the objectives of this work will be the (i) preparation of PMMA/TiO_2 duplex coatings on Ti dental implants, and (ii) measurement of electrochemical corrosion parameters of prepared coatings in fluoride-containing saliva.

2. Materials and methods

In this study, Ti-6Al-4V (Titanium grade 5) commercially dental implants were used as a substrate with a diameter of 3.5 mm and length of 13 mm from Tabriz Implant, Tabriz, Iran. Before the PEO process, implants were degreased in ethanol and ultrasonic bath for 5 min. PEO process was carried out on the dental implants using a pulsed direct current (DC) power supply KIKUSIU PWR800H (Japan). The PEO cell was composed of a stainless-steel tank with a cooling system as a cathode and the implants as an anode. The electrolyte consisted of...
an aqueous solution of 0.3 M of calcium acetate \((\text{Ca(C}_2\text{H}_3\text{O}_2\text{)}_2)\) (Merk) and 0.02 M of glycerophosphate disodium \((\text{C}_3\text{H}_7\text{Na}_2\text{O}_6\text{P})\) (Merk) in 500 ml of deionized (DI) water. The pH and conductivity of electrolyte were measured 5.21 and \((14.1 \text{ mS} \cdot \text{cm}^{-1})\), respectively. Metrohm 691 pH meter and Mettler Toledo Inlab 730 probe were used to determine electrolyte conductivity and pH values, respectively. A pulse voltage of 290 volts, a frequency of 250 Hz, a duty cycle of 60%, and an anodization time of 10 min were determined for PEO process [52]. Afterward, the implants were rinsed, air dried, and kept in the desiccator. Deposition of PMMA on PEO coated implants was performed using electropolymerization method that has been reported by E De Giglio et al for preparation of PMMA coatings on Ti-based substrates [53]. A schematic illustration of layers preparation by PEO and electrospray processes on Ti dental implant is shown in figure 1.

The initial surface examination of coated implants was observed by optical microscopy (Zeiss Axioskop2-MAT). The surface and cross-sectional morphology of coatings were analyzed using an FEI Nova Nanosem 440 scanning electron microscope (SEM, Leica Cambridge Ltd., Cambridge, England). The elemental distribution in coatings was analyzed using energy dispersive x-ray spectrometer (EDS, Oxford INCA energy) attached to the SEM. PHYNIX FN thickness meters were used to measure the average thickness of the coatings. At different regions, a roughness tester (PHYNIX TR-100) was used to measure the mean surface roughness \((R_a)\). The adhesion strength of coatings was measured in the outer part of the implants’ thread by an adhesion tester (PosiTest AT-A50) [55]. Phase crystalline structures of PEO coated dental implants were investigated by x-ray diffraction (XRD) using Cu Kα radiation \((\lambda = 1.54056 \text{ Å})\) in a 2θ scan ranging from 20 to 80°. Fourier transform infrared spectroscopy (FTIR) analysis of PMMA layers was conducted using a VERTEX 70, Bruker spectrometer, in the range of 4000–400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and a scan time of 55 s. Electrochemical measurements were used to detect differences in corrosion resistance among coated samples. The corrosion resistance was examined with open circuit potential (OCP) measurements, potentiodynamic polarization test (PDP) and electrochemical impedance spectroscopy tests (EIS) in saliva and fluoride-containing saliva solutions at 36.5 °C. An oral electrolyte was mimicked using Fusayama-Meyer artificial saliva [56]. The composition of the saliva solution is listed in table 1. According to table 1, Merck’s reagents with their CAS number were added slowly to the 1 l DI water to be used as received without any further purification. To simulate fluoridated media, 0.24 mol.L\(^{-1}\) sodium fluoride (NaF, Sigma Aldrich, USA) was added to the saliva solution. The electrochemical measurements were conducted using a potentiostat (EG & G, PAR, 263A, USA) in the conventional three electrode cell with specimen as a working electrode (W.E.), a platinum plate as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode (R.E.). To remove oxide from the uncoated dental implants formed by air, a cathodic pre-treatment of 1.2 V\(_{\text{SCE}}\) was performed before each test.

### Table 1. Amount of reagents for preparing 1 l of the saliva solution.

| Order | Reagent     | Amount (g.l\(^{-1}\)) | CAS Number |
|-------|-------------|-----------------------|------------|
| 1     | NaCl        | 0.4                   | 7647–14–5  |
| 2     | \(\text{Na}_2\text{HPO}_4\cdot2\text{H}_2\text{O}\) | 0.690         | 13472–35–0 |
| 3     | KCl         | 0.4                   | 7447–40–7  |
| 4     | \(\text{CaCl}_2\cdot2\text{H}_2\text{O}\) | 0.796         | 10043–52–4 |
| 5     | \(\text{Na}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}\) | 0.005       | 1313–84–4 |
| 6     | Urea        | 1.0                   | 57–13–6    |

**Figure 1.** Schematic illustration of preparation procedures of PEO and TiO\(_2\)/PMMA coatings on the Ti dental implant surfaces. Reprinted from [54], Copyright (2021), with permission from Elsevier.
for three minutes. To stabilize the OCP, the coated dental implants were immersed in saliva and fluoride-containing saliva solutions for 1 h before electrochemical measurements. The electrochemical impedances were measured by applying a 10 mV sinusoidal potential around $E_{\text{ocp}}$ at a steady state in the 100 kHz–10 mHz frequency range. A suitable fitting procedure implemented in ZView software was used to interpret the experimental results assuming an equivalent circuit. PDP curves were obtained at ±20 mV versus OCP with a potential sweep rate of 1 mV.s$^{-1}$.

3. Results and discussion

Ti dental implants were purchased as shown in figure 2. According to OM observation of the purchased dental implant, it was manufactured according to the design, without foreign matter and chips on the surface and large machining defects.

PEO treated specimens with highly porous surfaces are shown in figure 3 under low magnification SEM images. PEO coatings exhibit pores and cracks throughout their entire morphology, as shown by top surface images. The pore structure formed by the PEO treatment of titanium alloys is characteristic of the oxide layer [57]. PEO coated sample had pores ranging in size from 0.5 μm to 1 μm in diameter. In regards to the formation of pores and cracks, they were caused by gas evolution/molten oxide eruption in the discharge channel, and the thermal stress caused by rapid solidification of the molten materials in contact with the cool electrolyte, respectively. In the PEO process, when the applied voltage exceeds the voltage at which sparks need to appear on the surface of the substrate, microdischarges will form [30]. Afterward, the substrate material and the initially passive layer formed in the first stage of anodization partially melt due to the generated high energy by the electrical microdischarge. These molten materials erupt to the cool electrolyte from discharge channels like volcanoes [58]. The evolution of the microdischarges in different time of the PEO process of Ti dental implant is shown in figure 4. It is found that the size of microdischarges increases and the number of them decreases during the PEO process. In this study, at 1 min after the initial microdischarge appeared on the anodic surface, the breakdown voltage was recorded ($V_b$), and after 10 min, the final voltage was recorded ($V_f$). We recorded $V_b$ and $V_f$ at a voltage of 690 V and 745 V, respectively. Moreover, some elements may be incorporated into the molten

![Image](image-url)
substrate/oxide that came from the PEO electrolyte. These elements, mostly come from anions migrated to the positively charged anode, and can participate in the reactions that occur in the micro-discharge channels [59]. It has been reported that the electrolyte composition has a considerable effect on the intensity of sparks and microdischarges and thereby the size of formed pores [59]. As a consequence of this, it is important to note that the electrolyte’s properties such as chemical composition and conductivity play an important role in determining PEO coatings’ final composition and microstructure.

A majority of pores and cracks cause the PEO coating to have a poor layer of protection because of ions that penetrate through the PEO layer causing the coating to have weak-protective properties. As can be seen in

Figure 3. SEM micrographs of PEO coatings on the Ti dental implant in different magnifications.

Figure 4. Microdischarges evolution on the Ti dental implant in the different oxidation time.
Figure 5, the PMMA layers are depositing successfully on the PEO-pretreated surface of the Ti dental implants and are sealing the existing pores and cracks that are present in the PEO coating. Specifically, there were no evident defects in the appearance of the samples, such as micro-pores or micro-cracks, as they were examined. The composite coating formed from the mixture of TiO$_2$/PMMA as a result of sealing with PMMA presented a much flatter and more compact morphology after sealing with PMMA. The corrosion resistance of TiO$_2$/PMMA composite coatings can be greatly enhanced by an effective seal.

Table 2 presents the results of EDS point analyses of coatings. Basically, the PEO coating was composed mainly of O, Ti, Ca, P, C, and Na. There is a very high O content in the coating, which can reach up to 40.61%, higher than the contents of Ca and P elements in the coating, indicating that the PEO coating mainly consists of oxides that contain Ca and P. Elemental analysis of PMMA layer on the PEO-coated Ti dental implants demonstrates that carbon and oxygen elements are mainly from PMMA.

The thickness of the PMMA/TiO$_2$ coating was measured 44 $\mu$m, which is significantly higher than the thickness of the PEO coating (18 $\mu$m), to prevent the transfer of aggressive ions after the implant has been placed in the body. The cross-sectional morphology of PEO coating coated with PMMA layer is shown as figure 6. There were typically two layers in the entire coating, corresponding to the PEO coating and the PMMA layer. The roughness of PEO and PMMA/TiO$_2$ coatings was obtained 2.32 and 0.75 $\mu$m, respectively. The decrease in surface roughness is attributed to the seal of pores and cracks of PEO coatings by PMMA.

According to the XRD pattern of the coating of the PEO on Ti dental implants (figure 7(a)), the characteristic peaks can be identified as being composed of a small amount of rutile-TiO$_2$ (Reference code: 01–078–1510) and anatase-TiO$_2$ (Reference code: 00–002–0387) phases, which are the main constituents of the coating [62]. During the plasma process, Ti dental implant substrates are oxidized to produce rutile and anatase phases. A relatively low temperature is required for anatase to form and it is possible for it to transform into rutile at higher temperatures, which are stable at temperatures above 800 °C [63]. As a result of the x-rays penetrated through the PEO coating, Ti diffraction peaks are activated from within the substrate, because the x-rays are able to penetrate through the PEO coating and penetrate the Ti substrate through cracks and pores [64]. A FTIR spectrum of the prepared TiO$_2$/PMMA coatings is shown in figure 7(b). The FTIR characterization was used to confirm the presence of PMMA on PEO coating after electropolymorization by analyzing the special chemical bonds. The peak at 475 cm$^{-1}$ is attributed to TiO$_2$ compounds produced by PEO [65].

Carbonyl groups are the
main constituents of the polymers, with a band at 1722 cm$^{-1}$. There is a peak observed at 1064 cm$^{-1}$, which corresponds to the vibrations of the –C–O–C– bond. Other peaks occur at about 1248 cm$^{-1}$, which are attributed to the C–O bond’s stretching vibrations. The peaks showed at 1599 cm$^{-1}$ and 1725 cm$^{-1}$ are related to stretching of C=C, and C=O groups, respectively. There are also bands associated with CH$_3$ and CH$_2$ vibrational modes in the 1495–1280 cm$^{-1}$ spectral range. Peaks around 2953 cm$^{-1}$ and 2987 cm$^{-1}$ are identified to stretch mode of C–H groups [66].

At the electrode/solution interface, the variation of the potential of the time-dependent electrode is the first indicator of which reactions happening at the metal/solution interface due to the changes in the electrode potential [67]. Corrosion potentials near steady-state elaborate the metals’ passivation potential in solution determined by electrode kinetics and thermodynamics. Figures 8(a), and (b) show the OCP variations versus immersion time for samples in pure saliva and fluoride-containing saliva solutions, respectively. It can be seen that, samples’ OCP increase gradually in both solutions (figure 8) during the initial stage of immersion. Moreover, the near-steady state was reached after extending the immersion period for all samples in both media. An ongoing passive film in solution is typically responsible for such features [68]. During the passivation process, their $E_{ocp}$ values and pH values stabilized at around 320 mV$_{SCE}$ and 450 mV$_{SCE}$, respectively. A comparison of these variations once the uncoated implant was coated.
revealed that the simple and composite PEO coating shifted the potential in the direction of a positive value and increased the corrosion resistance of substrate. As it can be seen in figures 8(a) and (b), the OCP value of PMMA-PEO duplex coated implants are higher than that of simple PEO coatings in both media, indicating the better corrosion performance. In the time-dependent profiles in fluoride-containing saliva solution, potential fluctuations appear, likely caused by active metal dissolution. It has been reported that the pH and the existence of the fluoride ions in the electrolyte are the most significant determinants of the process of active dissolution and passivation of Ti in acidic solutions containing fluoride.

The corrosion protection properties of the coatings were evaluated using PDP tests. Figures 9(a), and (b) shows the PDP curves for Ti dental implants coated with PEO, PMMA, and uncoated implants in saliva and fluoride-containing saliva solutions at 36.5 °C, respectively. From the PDP curves, the corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel slopes were calculated directly by Tafel region extrapolation, while Stern-Geary equation was used to calculate polarization resistance values (R_p) \[69]\:

\[
R_p = \frac{\beta_a \beta_c}{2.3i_{corr}(\beta_a + \beta_c)}
\]

Table 3 lists all electrochemical parameters extracted from PDP curves. It is generally known that corrosion resistance can be determined by the combination of low I_{corr} and high E_{corr}. When compared with the uncoated dental implant sample, the E_{corr} of the coated samples increased, and the I_{corr} of the coated samples decreased as
well, because ceramic PEO coatings (TiO₂) are capable of blocking a significant amount of corrosive ions such as Cl⁻ and F⁻ in both media [70]. PEO coatings’ anticorrosion properties are determined by a combination of their thickness, roughness, porosity, and chemical composition [70]. It can be seen from table 3, the deposition of the PMMA layer gradually enhanced Ecorr and Icorr values as a consequence of increased coating thickness and reduced mean surface roughness, as we mentioned before. When a compacted PMMA layer is deposited on top of the PEO coating, the pores and cracks are sealed, preventing corrosive media from infiltrating the dental implant substrate through the pores and cracks [71]. Moreover, a decrease in Icorr and Rp was observed in fluoride-containing saliva compared to pure saliva. Therefore, the results indicate that samples exposed to fluoride-containing saliva medium have an increased corrosion rate.

AC impedance measurements were conducted on the samples to understand how PMMA layer contributes to electrochemical corrosion [67]. The following diagrams in figures 10(a), (b), (d), and (e) illustrate the Nyquist plots of uncoated and coated samples saliva and fluoride-containing saliva solutions at 36.5 °C, respectively. There are points on all plots representing the experimental data, and lines represent the result of the fitting for the experimental data. There can be a qualitative comparison between the corrosion resistance of the samples and the EIS spectra, indicating a higher corrosion resistance when the semicircles are larger and are associated with a lower frequency [71]. As shown by the larger radius of the capacitive loops of coated samples, compared with uncoated Ti dental implant alloy, coated samples provide higher protective efficiency. We analyzed the impedance data of coated and uncoated implant substrates using equivalent circuits shown in figure 10(c) and (f), respectively. An electrolyte resistance between a reference electrode (RE) and a working electrode (WE) is represented by Rs in the circuits proposed here. There are two kinds of resistance in the figure 10(f), the inner barrier layer (Ri) and the outer porous layer (Ro) resistances paralleled with their constant phase elements (CPE), e.g. CPEi and CPEo, respectively. A passive layer’s resistance and its phase element that intrinsically formed on the surface of uncoated Ti dental implant in both solutions are shown by Ro and CPEo in figure 10(c). CPEs were
Table 4. Calculated parameters of the EIS in the equivalent circuits.

| Sample          | EIS test’s solution       | $R_s$ ($\Omega$.cm$^2$) | (CPE-T)$_o$ ($S^\circ$.Ω$^{-1}$.cm$^{-2}$) | $n_o$ | $R_o$ (kΩ.cm$^2$) | (CPE-T)$_o$ ($S^\circ$.Ω$^{-1}$.cm$^{-2}$) | $n_i$ | $R_i$ (kΩ.cm$^2$) | $W_o$-R (kΩ.cm$^2$) | $W_o$-T (s) | $W_o$-P |
|----------------|---------------------------|--------------------------|---------------------------------------------|------|------------------|---------------------------------------------|------|------------------|---------------------|-------------|--------|
| Ti             | Pure saliva               | 24.43                    | $1.18 \times 10^{-3}$                       | 0.96 | 0.42             | ---                                         | ---  | ---              | --                  | ---         | ---    |
| PEO            |                           | 23.77                    | $1.24 \times 10^{-3}$                       | 0.83 | 8.16             | $1.64 \times 10^{-5}$                       | 0.81 | 15.35            | 8.95                | 0.31        | 0.33   |
| TiO$_2$/PMMA   |                           | 24.10                    | $5.12 \times 10^{-6}$                       | 0.94 | 18.24            | $3.55 \times 10^{-6}$                       | 0.84 | 24.22            | 12.59               | 4.1         | 0.12   |
| Ti Fluoride-containing saliva |   | 12.18                    | $0.19 \times 10^{-3}$                       | 0.97 | 0.12             | ---                                         | ---  | ---              | --                  | ---         | ---    |
| PEO            |                           | 11.52                    | $1.09 \times 10^{-3}$                       | 0.85 | 2.10             | $0.91 \times 10^{-5}$                       | 0.88 | 6.36             | 3.73                | 0.11        | 1.12   |
| TiO$_2$/PMMA   |                           | 12.08                    | $2.53 \times 10^{-8}$                       | 0.93 | 9.39             | $9.15 \times 10^{-5}$                       | 0.92 | 16.88            | 5.67                | 3.75        | 0.77   |
used instead of capacitances due to the non-ideal nature of the coatings’ system [72]:

\[
Z_{\text{CPE}} = \frac{1}{T(j\omega)^n}
\]  

(2)

where \( n \) is the exponential coefficient varied between 0 and 1, \( T \) is an angular frequency independent constant, and \( j \) is a unit of imaginary. When \( n = 1 \), CPE is the pure capacitance and when \( n = 0 \), CPE is the pure resistance. In figure 10(c), it can be seen that the equivalent circuit for coated implants characterized by two-time constants combined with a Warburg element. A Warburg open terminus \((W_o)\) indicates that corrosive agents diffuse through coatings on a semi-infinite basis. Nyquist plots clearly demonstrate a straight line at low frequencies, which is caused by Warburg impedance. Corrosion products that accumulate locally in defects probably caused this feature. This feature in equivalent circuit is consistent with Schott’s study [51]. A combination of the \( W_o \) and the \( R_i \) offered the best fit to the data in the present study. The observation indicates that ions diffused mainly near the interface between coating and substrate and the inner barrier layer. Equation (3) expresses \( W_o \) element mathematically [73]:

\[
Z_{W_o} = \frac{W_o-\text{R} \times \cot(j \times W_o-\text{T} \times \omega)^{W_o-\text{T}}}{j \times W_o-\text{T} \times \omega)^{W_o-\text{T}}}
\]  

(3)

The diffusion resistance and diffusion time are represented by \( W_o-\text{R} \) and \( W_o-\text{T} \), respectively. An exponential parameter, \( W_o-\text{R} \), ranges from 0 to 1. Based on equivalent circuits, table 4 presents the fitting parameters for the EIS spectra. It can be seen that corrosion resistance in both media is dependent on the inner barrier layer which can be observed by the lower values of \( R_o \) than \( R_i \) [74]. The results also showed that a decrease in the \( R_o \) and \( R_i \) values in the fluoride-containing saliva medium compared to the pure saliva. As a result of this observation, we can conclude that fluoride ions in acidic media can increase the corrosion rate. Comparatively to a simple PEO coating, the coating with a PMMA layer had increased resistance in its outer porous layer’s resistance. Because of the porous nature of the simple PEO coating, it is easily penetrated by corrosive media, making it susceptible to destruction by corrosion [71]. The PMMA layer is deposited over the PEO coating, causing the pores to decrease and electrolyte pathways to increase. Moreover, the decreases in porosity, as well as the increase in aggressive ions diffusion routes through the coating, are both responsible for an increase in \( W_o-\text{T} \) and \( W_o-\text{R} \) values by depositing the PMMA layer on the top surface of PEO coatings.

4. Conclusion

Ti-based dental implants treated with PEO process have a porous structure and contains a lot of microcracks. When PMMA layer was deposited on PEO-treated implant samples, pores and cracks were effectively sealed. Compared to pure saliva, the samples showed a higher corrosion rate in the fluoride-containing saliva medium. From greatest to least, the anticorrosive properties of the specimens in both media were as follows: TiO2/PMMA > PEO > dental implant substrate. In the acidic fluoride-containing media, the PMMA layer can provide a more effective barrier against the corrosive ions entering the PEO coating, resulting in significantly increased corrosion resistance of the Ti dental implants. These results may shed light on some potential clinical complications related to the corrosion behavior of dental implants in harsh service conditions.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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