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Electrostatic Deposition of Poly(Methyl Methacrylate)/Titanium Carbide Coatings on Austenitic 316L Stainless Steel Implant

Ghofran Dhafer*, **Mohanad N. Al-Shroofy**, **Hanaa A. Al-Kaisy**

Materials Engineering Dept.,University of Technology-Iraq, Alsina'a Street, 10066 Baghdad, Iraq.
*Corresponding author Email: mae.19.20@grad.uotechnology.edu.iq

HIGHLIGHTS

- Applying a PMMA-based composite coating with TiC particles as reinforcement.
- Using the electrostatic spray method as a dry coating method for biomedical applications.
- Study the morphological characteristics of the applied coatings.
- Identifying the biological activity of PMMA/TiC coatings by determining the corrosion resistance and the wetting behavior.

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ABSTRACT

316L stainless steel alloys are extensively used in orthopedic applications for the fixations and substitutions of defective bone tissues in the human body because of their excellent combination of mechanical and biological behavior. However, just like other metallic implants, they tend to release some toxic ions that may lead to serious health issues. Therefore, this study attempts to increase the alloy's resistance against corrosion while maintaining its good mechanical properties by applying a modified coating layer of PMMA-based composites titanium carbide as reinforcement material using dry electrostatic spray deposition (ESD) under constant conditions (25 kV, 15-20 cm distance, compressed air of 15 psi, and spraying angle about 45.0o for 3 0sec). The titanium carbide was added with ratios of (5, 10, 15, 20) wt. % respectively. The coatings' surface morphology and phases were studied using Field Emission Scanning Electron Microscope, Energy-dispersive X-ray spectroscopy, and X-ray diffraction. Also, the biological behavior of the composite coated samples was studied by investigating their corrosion and wetting attributes. The results revealed that homogenous, uniform, crack-free coating layers and high surface wettability were obtained. Indicating the suability of PMMA/TiC for biomedical applications due to the alloy's improved corrosion resistance and biocompatibility.

1. Introduction

Due to its high corrosion resistance, mechanical properties, and biocompatibility, 316Lstainless steel alloy has been used as an implant in various areas of the human body as it forms a thin film of Cr_2O_3 on its surface. Still, it also tends to release some toxic ions like (Ni & Cr) when it comes in contact with the Cl-, Sulfuric compounds, etc., contained in the fluids inside the human body and the poor adhesion with surrounding tissues [1]. Therefore, numerous studies have focused on improving implant bioactivity, cytocompatibility, and acceptance inside the human body without side effects [2,3,4]. Oláh et al. in 2016 coated different metallic implants (T-64 and Co-Cr) with a titanium carbide layer using magnetron sputtering, the mechanical, structural, and electrochemical behaviors of the coatings were characterized, and the results revealed that the life of implants is extended [5]. Kao et al. used the magnetron sputtering method to apply a titanium carbide layer over the 316L SS alloy surface. It investigated the corrosion behavior of the applied coatings in biological environments. As a result, improved wear and corrosion resistance with enhanced alloy biocompatibility [6]. Umar et al. in investigated the biological activity of the carbide coatings by fabricating a thin coating layer of ZrC and TiC over the 316L SS using the magnetron sputtering technique. The corrosion behavior was studied in the solution of artificial bone plasma, bacterial adhesion against P.aeruginosa, and the adsorption of blood proteins. The final results indicated that high corrosion resistance of the coated samples, lower adhesion of bacteria, and high adsorption of proteins were achieved [7]. Scandurra et al. [8] investigated the ability of titanium carbide to enhance implant bioactivity. This was achieved through promoting osseointegration and cell growth by fabricating a thin coating layer of graphitic carbon whose compatibility is enhanced using TiO_2 and TiC using plasma-assisted ion plating.

The results of the cellular adhesion test showed good cell adhesion. Upon implanting in rabbits, a good bone attachment was observed [8]. Hosseini et al. in 2021 deposited a nano Hydroxyapatite-Silicon Carbide coating on 316LSS using the electrophoretic technique, and the corrosion resistance was measured in SBF. They found that HA with 3% SiC coating gives the optimized requirements, with a low micro-cracks level compared with other coatings [9]. In 2021, Issa et al. fabricated a thin film of PMMA-based composite coating with various bio-ceramic materials as reinforcements using an electrostatic

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deposition [10]. FESEM & EDS were used to study the surface morphology; the coating hardness and adhesion were studied using mechanical tests. The results indicated that a uniform, crack-free coating film with enhanced mechanical characteristics was achieved. This study aims to fabricate a PMMA/TiC composite coating using electrostatic spray deposition and study their morphological and biological characteristics.

2. Theoretical Section

Because of their superior mechanical properties, cyto-compatibility, &corrosion protection, metals are considered the best bio-materials for orthopedic applications. Titanium and its alloys, cobalt-chromium alloys, magnesium, and 316L SS are the common metallic materials used for medical implants. The latter is widely used. This is because, compared to others, austenitic stainless steel has the lowest cost with high biocompatibility and other biological requirements [11, 12]. Biocompatibility is highly affected by the corrosion attitude of material. Hence, greater potential for negative effects can be anticipated with higher corrosion rates. Metallic biomaterials corrode by releasing ions (Co, V, Al, Cr, and Ni) into the human body, which causes allergenic, toxic/cytotoxic, or carcinogenic effects [13,14]. Many factors can cause implant failure, could be mechanical, electrochemical, biological, or a combination of them. The mechanical factor includes the overloading, wear, and fatigue, while the electrochemical one is presented by the corrosion problems. Inflammation, infection, and enzymatic degradation may cause biological failure [1,2,15]. Biologically active coatings on implants can aid in achieving biocompatible surface protection. Biocompatible materials like hydroxyapatite [16], niobium oxide [17], and polymers like PMMA and chitosan [18,19] can be used for implant coatings. Lately, titanium carbide has been investigated as a possible candidate for corrosion coatings and is used to modify the surface activity against corrosion [20]. In the last years, it has been observed that transition metal carbides have properties that seem to be attractive for biomedical applications like excellent inertness to the body fluids, high compatibility, excellent protection against wear and corrosion, and tribological properties [21]. Among many carbides, Titanium carbide has superior biocompatibility and outstanding tribological characteristics, as revealed in several publications. They promote the adherence of artificial plasma proteins, resulting in quick and moderate osseo-integration [20,21,5]. Despite that, the behavior of TiC implant coatings in the corrosive and biological environments, on the other hand, is not fully understood. As a result, research into the corrosion, protein adsorbents, and microbial adherence characteristics of TiC coatings, which are critical for biomedical implants, is worthwhile [7]. Several applications of poly-acrylics included the usage of thin films for protective coatings. The developed attention in PMMA-based coating applications to enhance the resistance against corrosion of the implant is contributed to the polymer's superior chemical stabilization. Extensive research has revealed that PMMA-based composites are particularly appealing for surface modification of bio-implants. Since in addition to encouraging osseointegration, these coatings offer additional compatibility, biological activity, antibacterial properties, and corrosion resistance [22,23]. Many coating techniques have been used in the medical field, but recently electrostatic spray deposition (ESD) gained attention as a dry coating method for implants. ESD has gained traction over other powder deposition techniques due to its unique benefits, including short deposition time, energy savings, and a significant decrease in operational costs [24,9,25].

3. Materials

The main materials used in this work involve the following:

3.1 Substrate Material:

Austenitic 316L SS alloy plates with dimensions of (20x 20 x 1mm) represent the metallic substrate that has been used to be coated in this study.

3.2 Coating Materials:

The coating is made from a composite layer consisting of Poly (methyl methacrylate) as the matrix material with different concentrations of Titanium carbide as the reinforcing elements.

3.2.1 Poly (methyl methacrylate):

PMMA $(C_5O_2H_8)_n$ is a thermoplastic polymer with good thermal stability, mechanical properties, and high biocompatibility, and it can encourage osseointegration relatively. It is obtained by (Spofa Dental) company in Jičín, Czechia, with a mean particle size (of 4677.4nm).

3.2.2 Titanium Carbide

Titanium Carbide (TiC) is a highly biocompatible ceramic that was obtained from Alpha Aesar company in zlthe united states with a mean particle size of (718.6nm) and a cubic crystal structure.

4. Experimental Part

The substrate surface was mechanically ground with emery paper 80,100, and 150 grades to increase the surface roughness. After that, the plates were cleaned from rust, washed with deionized water, degreased with acetone, and dried before use. The preparation was carried out following the "ASTM Metals Handbook"[26]. Composite mixtures of the coating powders were made with different concentrations of PMMA: TiC, i.e. (95:5, 90:10, 85:15, and 80:20 wt %). The powders were then dryly mixed with a ball mill for 40 min. The coating layers were applied using the electrostatic spray method for (30sec) with (25Kv), (15-20cm) distance between the nozzle tip and the specimen (15psi) compressed air, and (45.0^o) spraying angle. The coated specimens were placed in an electric oven and cured at (160°C) for (1hr) for the film formation, the coating characterizations were obtained after cooling them at room temperature.

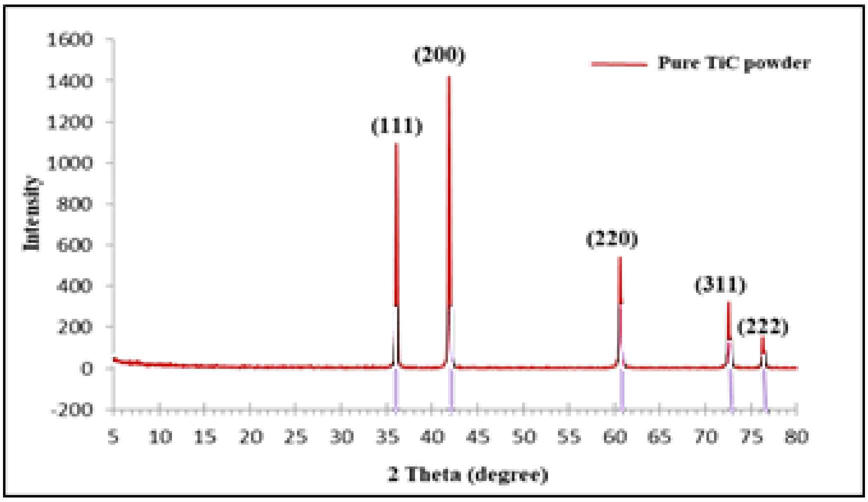

Figure 1: XRD Pattern of titanium carbide powder

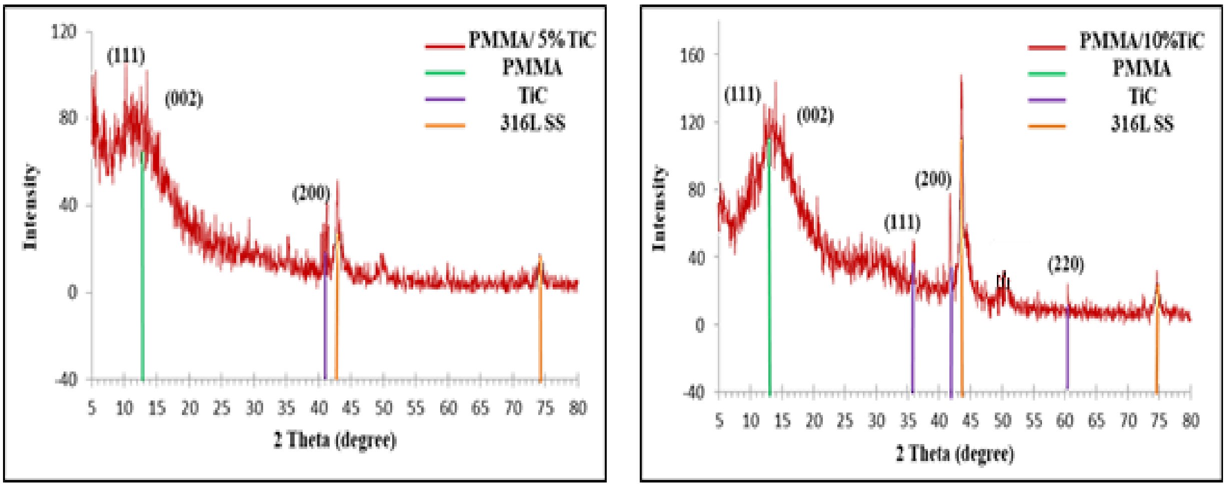

Figure 2: XRD Pattern of PMMA-based coatings with (5,10)wt% TiC, respectively

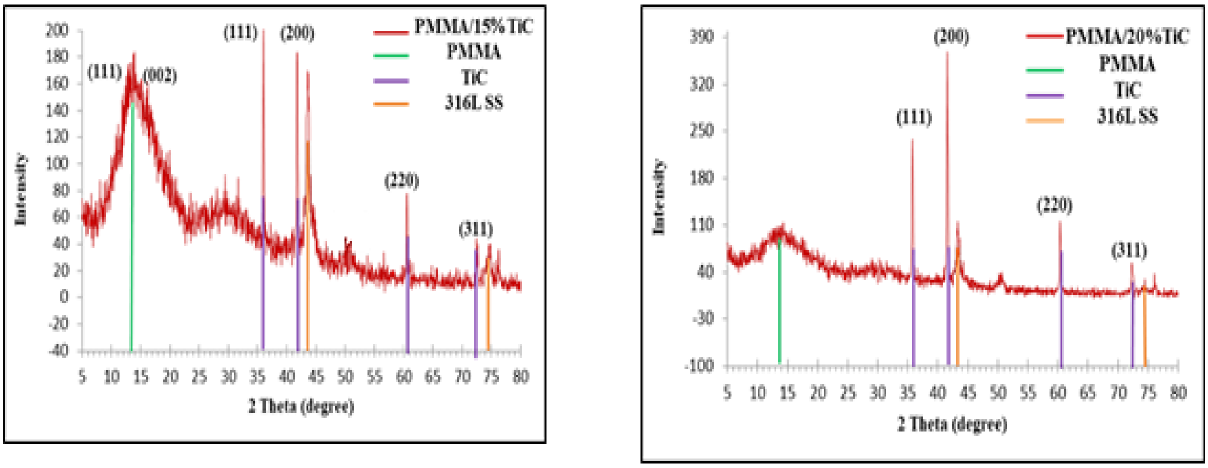

Figure 3: XRD Pattern of PMMA-based coatings with (15,20)wt% TiC, respectively

5. Results and Discussion

5.1 X-Ray Diffractions (XRD)

The XRD pattern of the pure TiC powder is shown in Figure1 and showed good agreement with the standard peaks in JCPDS files no. (65-7994), where the highest peaks were at two-theta = 36°, 42.1°, 60.9°, 72.8°, and 76.5° indicating the planes (111), 200, 220,311, and 222, [27]. Generally, the XRD patterns of all the coated specimens indicated the 316L SS alloy through the presence of highly intense peaks at 43.5°and 74.5°. Broad peaks have appeared at 13.6°, 14.8°, and 30.7° bands exhibited by the PMMA matrix, indicating their amorphous nature. Broad peaks have appeared at 13.6° and 14.8° bands exhibited by the PMMA matrix, indicating their amorphous nature. The highest peak intensity was at 13.6° and 14.8°, corresponding to the 111 and 002 planes, whereas the broad humps reveal the presence of PMMA crystallites with small dimensions [28, 29]. The same indication was detected for all the coated alloys except the 20%TiC sample. For the 5%TiC, only a low intense broad peak at 42° of two-theta related to the (200) plane has appeared. With continuous carbide addition, more intense plans tend to start appearing, thus reducing the amorphous nature of coatings. The 111 and 220 plans tend to appear in 10% TiC along with 36 ° and 60.7 ° peaks, and (311) plan along with the 72.8° appears in the the15%TiC, while XRD spectra of the 20% TiC coating showed that the PMMA humps are highly reduced indicating the reduced amorphousness of the coating. XRD patterns of PMMA/TiC coatings are shown in Figures 2 and 3. The XRD patterns indicated the amorphous nature of the coatings, denoting that the incorporation of the ceramic particles had no effect on the PMMA structural properties and no chemical reactions occurred between them.

5.2 Morphological Analysis (FESEM/EDS)

FESEM/EDS analysis of the coated specimens is shown in Figures 4 and 5. The SEM images revealed a uniform integration and distribution of the ceramic particles through the PMMA matrix with a homogenous coating deposition, i.e., no major cracks were obtained. It is important to mention that the PMMA particles retained their spherical shape after being deposited and cured because they weren't fully melted during the heating process for the film formation. The surface morphology of thin films showed that various shapes of the ceramics are embedded in the PMMA matrix from clusters of TiC particles distributed over the film surface. The EDS analysis shown in Figure 5 revealed that the Ti content was increased gradually at 3.23 wt%, 5.08 wt%, 7.9wt% and 9.86 wt% with decreasing in C content (70.33, 68.6, 67.6, and 66.76) wt% through the different concentrations of TiC (5,10, 15, and 20) wt% respectively. EDS mapping of the composite coatings is presented in Figures 6 and 7 below, showing the elemental distribution of the coating constitutes. Moreover, the cross-sectional images of the coated specimens, shown in Figure 7, revealed a crack-free coating film and homogeneous adhesion with a high degree of surface roughness.

5.3 Contact Angle Measurements

Nearly all studies have verified that surface hydrophilicity plays a crucial role in promoting the early stages of cellular migrations, proliferation, differentiation, and bone growth [30]. Generally, the wetting behavior is shown in figure 9.

Figure 10 indicates the contact angle measurements of all the coated specimens after (30sec) depositing a drop of water over the sample's surface. In general, the initial CA of coatings is below 90° and the drop has been almost completely dispersed and absorbed by the coating layer in all samples, indicating a high wettability. However, for the coatings containing TiC contained, the absorption was slower and took about (1-2) min for the drop to be diffused.

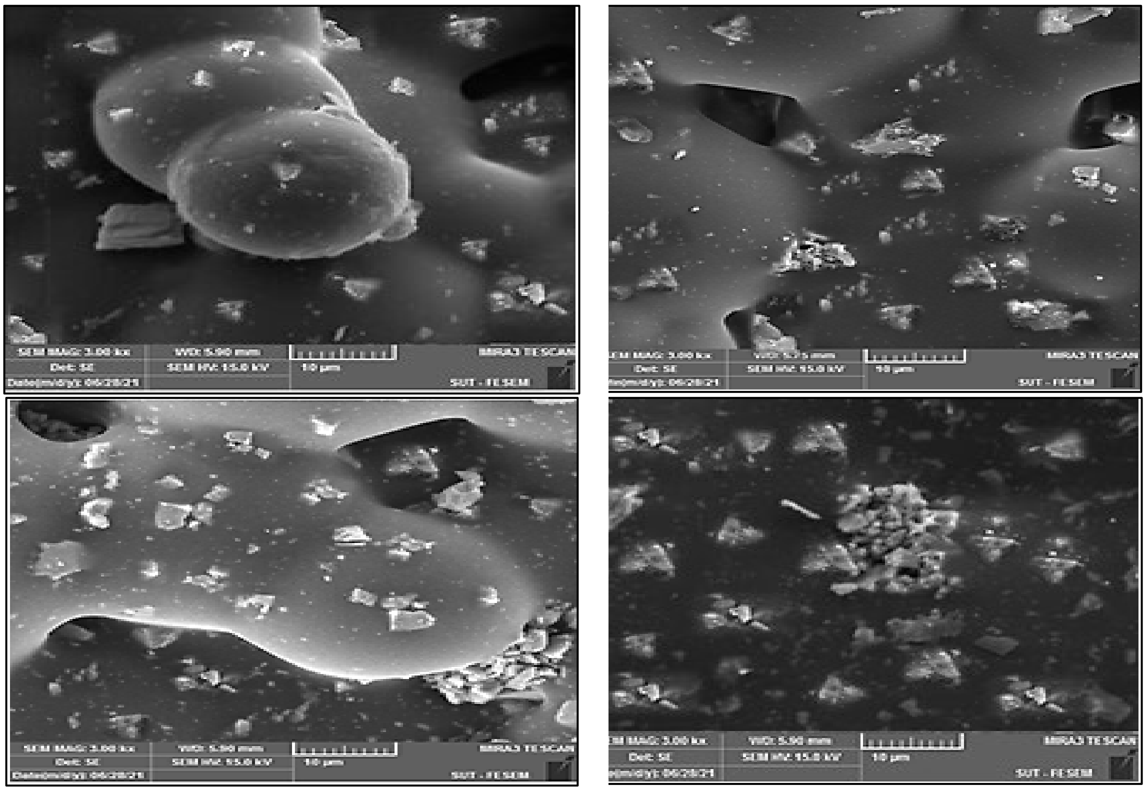

Figure 4: FESEM images of PMMA/TiC coatings a)5 wt%, b)10 wt%, c)15 wt%, and d)20 wt%

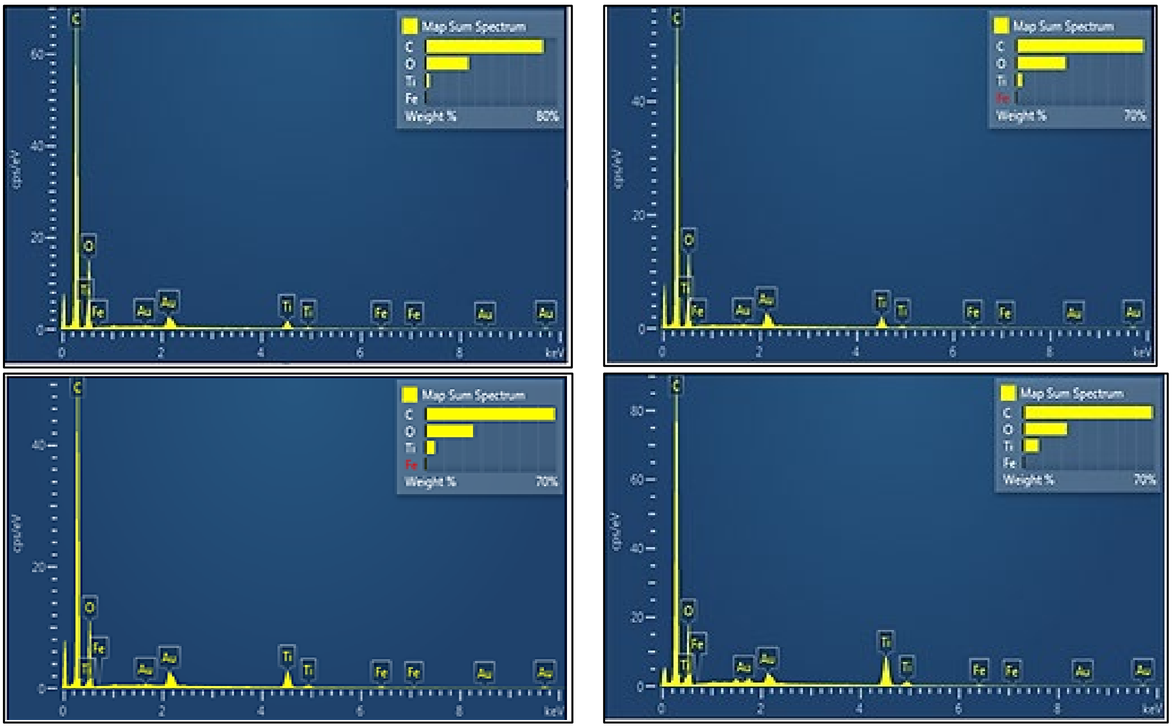

Figure 5: EDS analysis of PMMA/TiC coatings a)5 wt%, b)10 wt%, c)15 wt%, and d)20 wt%

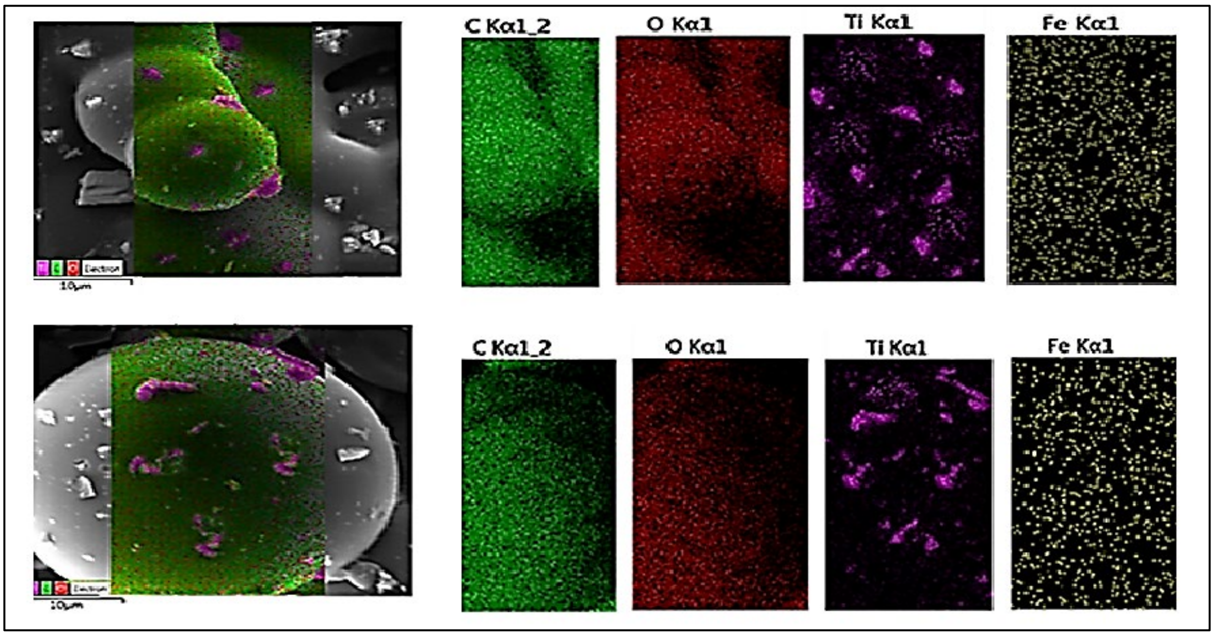

Figure 6: EDS mapping image of PMMA/TiC coatings a)5 wt%, b)10 wt%

5.4 Ion Release Test

The coated specimens were soaked in simulated body fluid for 30 days and incubated at 37 ^{o}C. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of specified chemical elements in the soaking solution by evaluating the optical radiation absorbed with a unique wavelength to each free atom.

Nickel and Chromium ions are the main toxic ions that tend to be released from the 316L SS when it comes in contact with the biological fluids. After 30 days of soaking the pure alloy in SBF at 37oC, it was found that their concentrations were about 2 ppm and 1.2 ppm, respectively. Although these might be considered very small concentrations, the human responses towards them may vary from one to another, causing different ranges of sensitivity and inflammations. As for all the coated specimens, the releasing of Ni and Cr ions was prevented, indicating the high improvement in corrosion resistance of the alloy, thus improving its biocompatibility.

The coating degradation and Osseo integration were also examined by determining the Ti and Ca ions after 4 weeks of soaking, as shown in table 1. The Ca concentration was decreased from 100.2 to 20.03, 22.9, and 25.6ppm after 4weeks. This decrease may be contributed to the reduction of calcium ions to form the apatite layer. It is also shown that the highest concentration of Ti ions released is indicated for the 15% TiC coating.

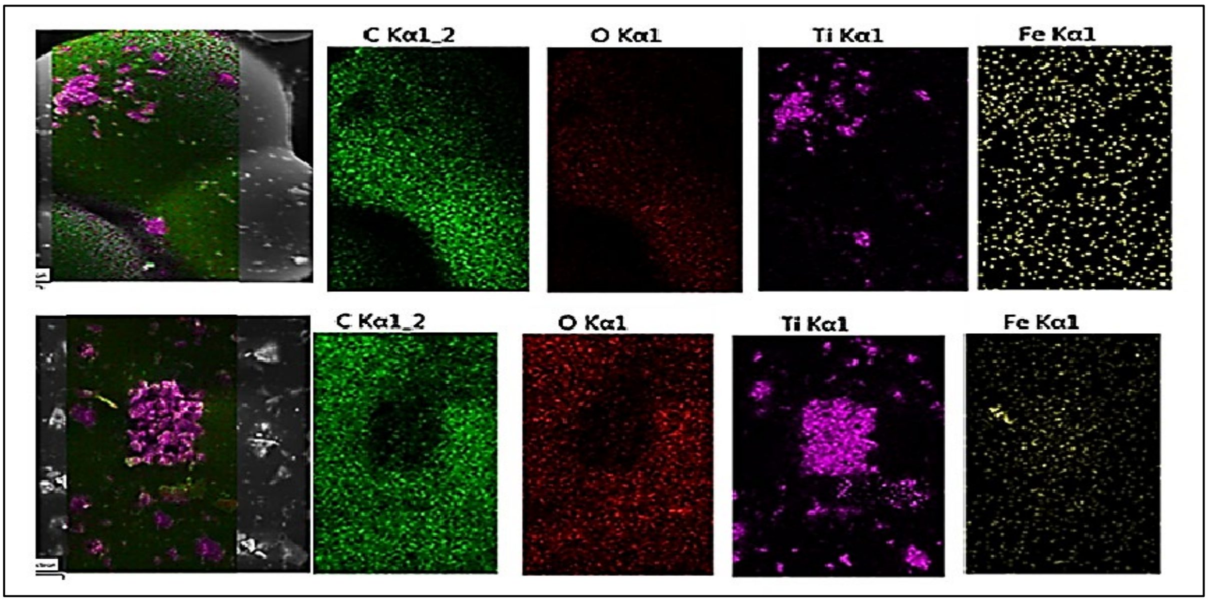

Figure 7: EDS mapping image of PMMA/TiC coatings a)15 wt%, and b)20 wt%

Table 1: Concentrations of released ions after immersion in SBF

	Ni(ppm)	Cr(ppm)	Ca(ppm)	Ti(ppm)
Time	4weeks			
Pure 316LSS	2	1.2	-	-
5%TiC	0	0	20.03	8.2
10%TiC	0	0	22.9	10.3
15%TiC	0	0	25.6	12.4

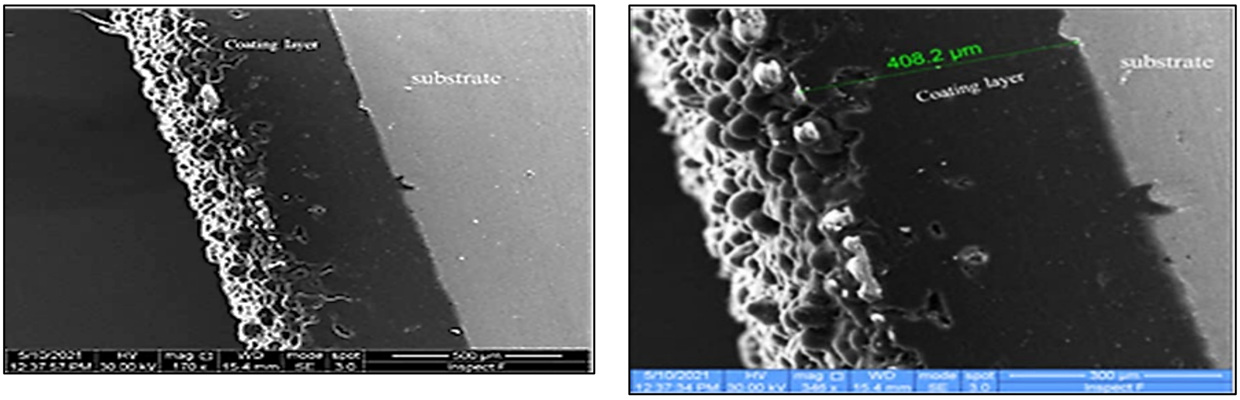

Figure 8: Cross-sectional FESEM images of the coated specimens

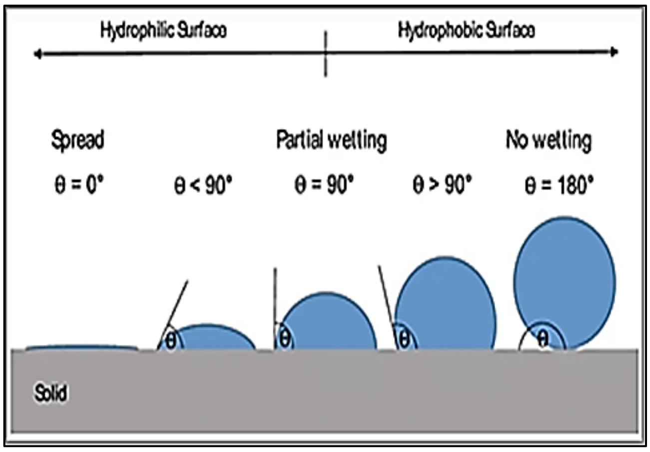

Figure 9: Wetting behavior explanation using contact angle [31]

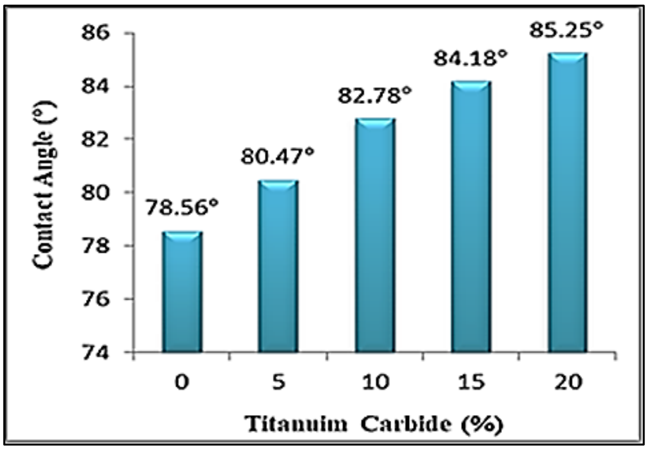

Figure 10: Contact angle test results after 30 sec for PMMA-based composite coatings

6. Conclusions

PMMA-based composite coatings were successfully applied using dry electrostatic deposition under 25 kV for 30sec, where the coating process possessed high cost-effectiveness and acceptable environmental impact. XRD analysis confirmed the absence of any chemical reaction between the composite components. SEM micrographs revealed desirable coating morphological requirements where a crack-free and homogenous coating with a uniform distribution of the reinforcement particles was obtained. Measured contact angles of the coated substrates revealed high wettability of the coating layers due to the hydrophilic nature of PMMA combined with TiC, which is considered a good indication of the biological behavior inside the human body. Furthermore, toxic Ni and Cr ions were prevented, indicating the high improvement in corrosion resistance of the alloy, thus improving its biocompatibility.

Author contribution

All authors equally contributed to this work.

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Data Availability statement

The data supporting the study’s findings are fully accessible upon request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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