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Structural and Morphological Characteristics of PEKK-Coated Titanium Disks by RF Magnetron Sputtering for Implant Osteointegration Application

Pure grade II titanium disks were coated with a thin coating of polyetherketoneketone (PEKK) polymer by RF magnetron sputtering using either nitrogen or argon gas. Sputtering technique was employed at 50 W for one hour at 60°C with continuous flow of nitrogen or argon gas. Field-emission scanning electron microscopy (FE-SEM) showed a continuous, homogeneous, rough PEKK surface coating without cracks. In addition, cross-sectional FE-SEM revealed an average coat thickness of 1.86 µm with argon gas and 1.96 µm with nitrogen gas. There was homogenous adhesion between the coating layer and substrate. The elemental analysis of titanium substrate revealed the presence of carbon, titanium, and oxygen. The RF magnetron sputtering with argon or nitrogen gas coated the titanium substrate with PEKK to provide a uniform coating thickness with increased roughness and wettability resulting in a more advantageous surface for implant osteointegration.

***Keywords*:** Polyetherketoneketone; Titanium; Magnetron sputtering; Coating
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1. Introduction

Titanium (Ti) and Ti alloys are commonly exploited for dental implants because of their corrosion resistance, biocompatibility, strong mechanical qualities, no cellular toxicity, and associated with minimal inflammatory responses in peri-implant tissues [1,2]. One significant drawback of Ti and its alloys is their dark grayish hue and the susceptibility to cellular sensitization when exposed to saliva and fluoride. This attributes to the observed galvanic action. In addition, the elastic moduli of the surrounding bone tissue are considerably lower than those of the Ti implant. These can increase the risk of mechanical stress on the bone and cause harm to the neighboring bone tissue, eventually leading to bone loss [3-5].

The primary function of a coating substance is to provide protection for bodily organs against the potential release of metal ions from metallic implant components. The coating substance's primary function is to protect the underlying metallic implant material and prevent metal ion release from the material into the body. Numerous coating methods were used to change the surface of dental implants for enhancement of osteointegration and biocompatibility, particularly for subjects with delay in healing of their bone [6]. In addition, the treatment of the implant surface could be utilized to enhance the wettability, change the surface topography, change the surface energy, increase cell proliferation, and accelerate the osseointegration process [7].

A method for efficient deposition of different types of thin films of materials is the radiofrequency (RF) magnetron sputtering. The target in the magnetron sputtering device is surrounded by a powerful magnetic field which leads to a spiral path of follow of electrons along the magnetic flux lines that surround it [8]. It is necessary to limit the plasma near the target to prevent any damage to the thin layer that forms on the surface [9]. The stoichiometry and uniformity of the film's thickness can be better maintained in this way [10,11]. Furthermore, RF magnetron sputtering, unlike other coating techniques, enables the deposition of coatings on ceramic, polymeric, and metallic implant materials [12-15].

The good and prospective biomechanical properties of PEKK, including its compressive, tensile, and flexural strength, have led to its increased use in dentistry and medical applications. The material's molecular structure, when modified with ketone groups (Fig. 1), is more versatile than PEEK in terms of surface alterations, bonding, and melting temperature [16,17]. In a simulated intraoral setting, PEKK possesses shock-absorbing characteristics and an elastic modulus that is quite comparable to bone [18]. Processing PEKK only modifies their form but their chemical characteristics remain unchanged. Additionally, PEKK does not have residual monomer in its composition nor does it have any porosity. It has a high melting point (T_m) ranging from 360°C to 388°C and a glass transition temperature (T_g) of 156°C [17,19,20].

This study utilized RF magnetron sputtering deposition to generate a thin coating of PEKK on grade II commercially pure Ti implant substrate. The effects of this coating in association with nitrogen (N) or argon gases (Ar) were investigated in vitro. The null hypothesis was that PEKK coating on commercially pure Ti does not improve the surface properties of Ti substrate for dental implant use. The alternative hypothesis was that PEKK coating on commercially pure Ti may enhance the surface properties of the Ti substrate for dental implant use.

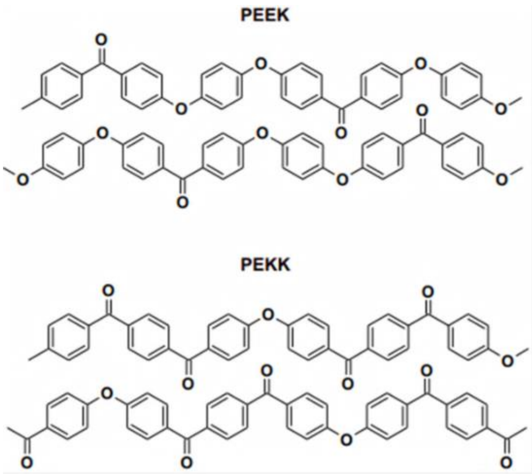


Fig. (1) The chemical structure of PEEK and PEKK [17]

2. Materials and Methods

Disk-shaped substrates with a diameter of 10 mm and a thickness of 2 mm were fabricated using grade II commercially pure titanium (CP Ti) rods of 99.9% purity. These rods were obtained from Orotig S.p.A. Co. (Italy) and were cut using a wire cutting machine manufactured by Knuth Smart DEM (Germany).

The surface treatment was started with the polishing of the specimens using a silicon carbide polishing paper with grit sizes of 500, 800, 1200, 2000, and 2400 in sequence. Then, the surface of the specimens was cleaned using 100% ethanol in an ultrasonic cleaning apparatus for 15 minutes. Subsequently, they were immersed in distilled water for 10 minutes. The disks were finally dried by exposure to air [3,10].

The CP Ti disks were divided into 3 main groups which are:

1. Group C: Ti disks without any PEKK coating.
2. Group Ar: Ti disks coating with PEKK by using RF magnetron sputtering with argon gas as a sputtering gas.
3. Group N: Ti disks coating with PEKK by using RF magnetron sputtering with nitrogen gas as a sputtering gas.

The magnetron sputtering PEKK targets, measuring 50 mm in diameter and 3 mm in thickness, were prepared by pressing the PEKK polymer powder in a pressing machine under pressure of 6 tons for 10 minutes.

The coating technique made use of a magnetron sputtering apparatus manufactured by Torr International Inc., (USA). In this system, the PEKK sputtering target was fastened to the cathode. The CP Ti substrates were connected to the anode on a rotating disk. The base was rotated at steady speed, so that all surfaces of the discs received an equal amount of PEKK material from the target. The previously mentioned process was conducted after the chamber was evacuated from air and either argon or nitrogen gas was pumped in, according to the specified test group. To clean the target surface and provide stable sputtering conditions, a pre-sputtering pressure of 1.5×10^{-3} mbar was applied [10]. The sputtering time, substrate temperature, target-to-substrate distance, working pressure, and magnetron power are summarized in table (1).

Table (1) The parameters of RF magnetron sputtering used for PEKK coating

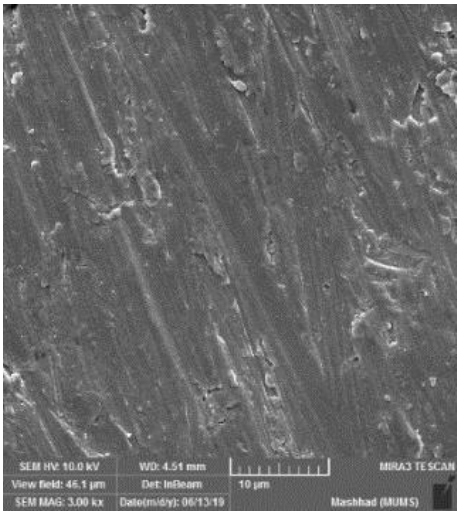
Gas	Power (W)	Pressure (Torr)	Substrate Temperature (°C)	Target-to-substrate distance (cm)	Deposition time (min.)
Argon	50	0.03	60	10	60
Nitrogen	50	0.03	60	10	60

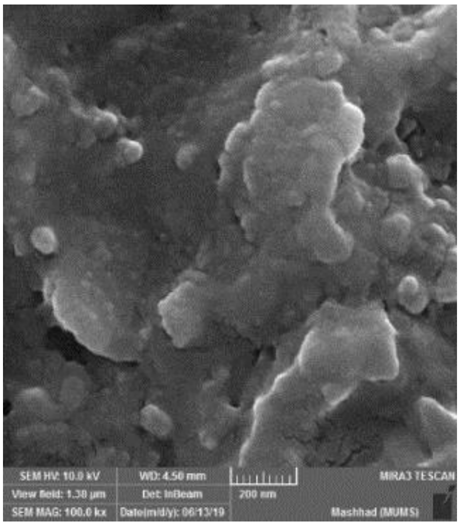
The thickness of the PEKK coating and surface topography were examined using MIRA3 TESCAN FE-SEM instrument (Czech Republic) once the coating procedure was finished. For elemental analysis, energy-dispersive x-ray spectroscopy (EDX) was employed. The surface wettability was evaluated using the contact angle measurement instrument (Creating Nano Technologies Inc., Taiwan). A Nanoscope atomic force microscope (USA) was used to measure the surface roughness. A SHIMADZU XRD-6000 X-ray diffractometer (Japan) was used for the phase study.

3. Results and Discussion

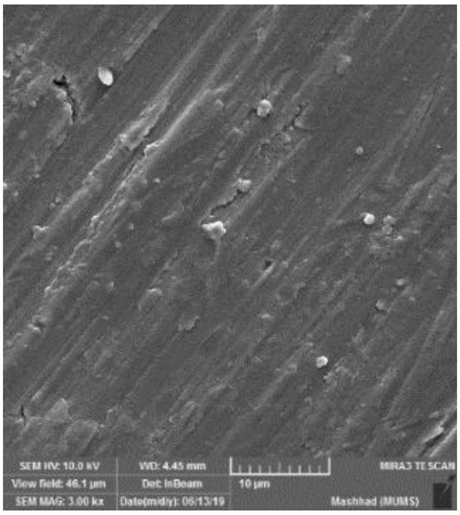
The limitations of metallic implants to form a harmonious relationship with the adjacent bone is a prevalent limitation. The differences in the chemical compositions of the two materials are the cause of the disparity between human bones and metallic implants. Surface coating is effective in improving osseointegration and managing the constraints of metal-based implants, including the release of harmful ions, corrosion, and wear [21]. Coatings that are both continuous and crack-free are indicative of healthy biological interactions between biological and synthetic tissues [10].

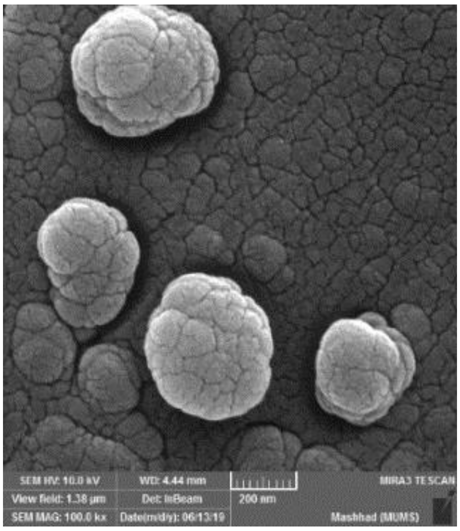
In the current study, Ti substrates covered with PEKK were analyzed using FE-SEM at two different levels of magnification. The surface morphology of the PEKK coating (Fig. 2) revealed a continuous and crack-free appearance, with uniformly dispersed PEKK particles and a few aggregates of varying sizes. The average coated layer thickness for group Ar was 1.86 μm, whereas for group N, it was 1.96 μm.





Group Ar





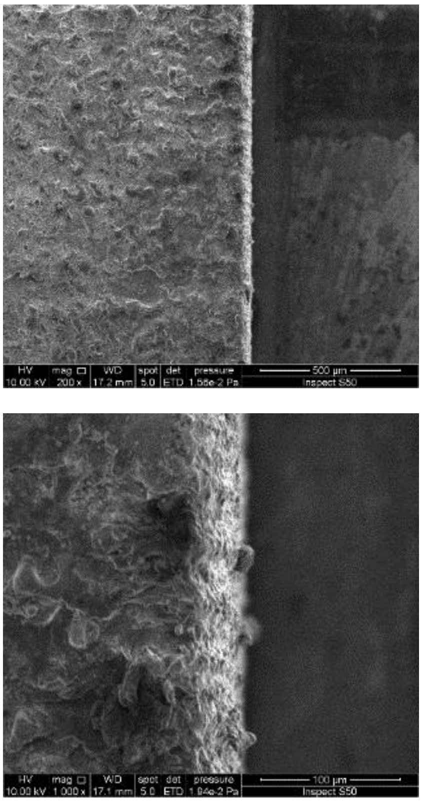
Group N

Fig. (2) FE-SEM images of Ar group and N group specimens at two magnifications

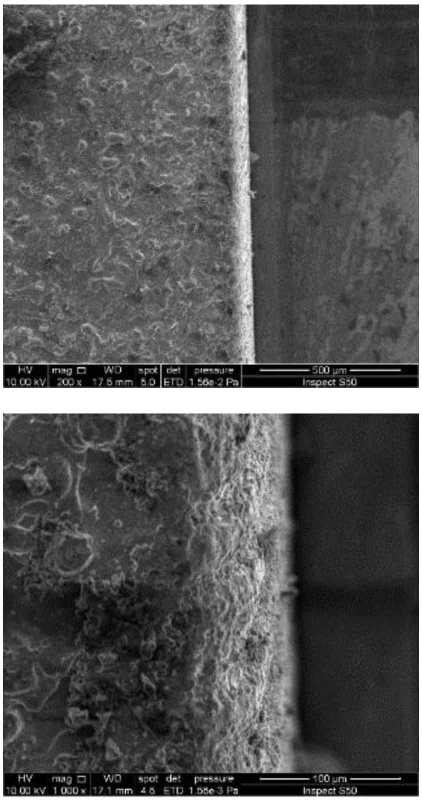
The FE-SEM images showed that the Ti substrate was efficiently surrounded by the PEKK particles, resulting in PEKK particles being bonded to the surface layer of Ti firmly without any gaps. A considerable amount of ketone groups is present in the surface structure of PEKK and this greatly enhances the ability to undergo changes in the surface chemistry. Thus, leading to the formation of a surface with small irregularities, greater surface area, and complex surface structure. These surface characteristics have significant effects on cellular behavior and the process of osteointegration on the PEKK surface [22,23].

The FE-SEM images revealed a highly uniform coating layer with good adhesion to the Ti substrate and no obvious flaws such as micro-cracks and pores (Fig. 3). The coating layer that is only a few micrometers is considered an optimal coating and is adequate for avoiding cracking and obtaining the desired effect for osseointegration [24,25].

The EDX investigation of the Ti surface showed Ti and oxygen (O) on the surface and the carbon (C), O, and Ti on the outer layer of the PEKK. Additionally, small amounts of nitrogen (N) were found on the specimens coated with PEKK in the N group and the specimens were not contaminated by any other components, as seen in table (2) and Fig. (4). The chemical composition of the coating material remained unchanged throughout the sputtering procedure. Also, the PEKK material did not undergo thermal deterioration after exposure to one hour of sputtering, thus avoiding a potential factor that might impact its biocompatibility.



Group Ar



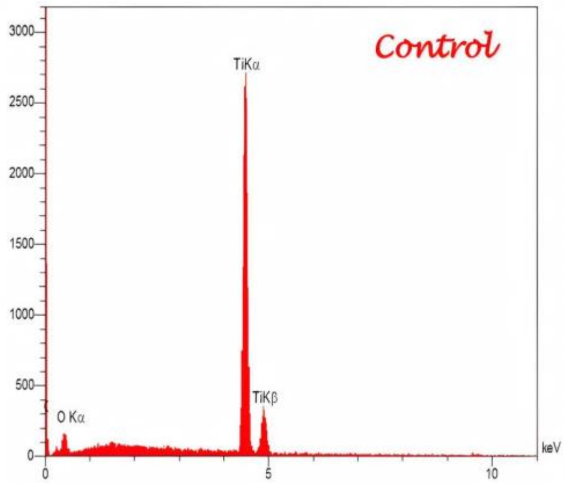
Group N

Fig. (3) The cross-sectional FE-SEM images of the CP Ti specimen coated with PEKK

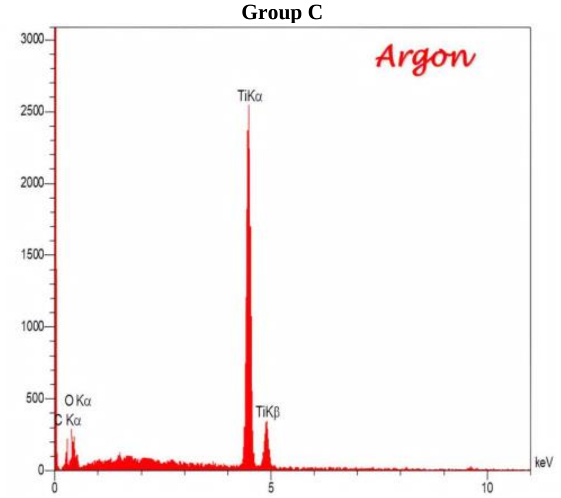
Table (2) Chemical analysis of the study groups

Element	Group C		Group Ar		Group N	
	W%	A%	W%	A%	W%	A%
Ti	96.24	91.72	61.95	35.72	60.1	34.30
O	3.76	8.28	23.85	38.29	25.01	39.48
C	-	-	14.20	25.99	13.09	24.92
N	-	-	-	-	1.8	1.3
Total	**100**	**100**	**100**	**100**	**100**	**100**

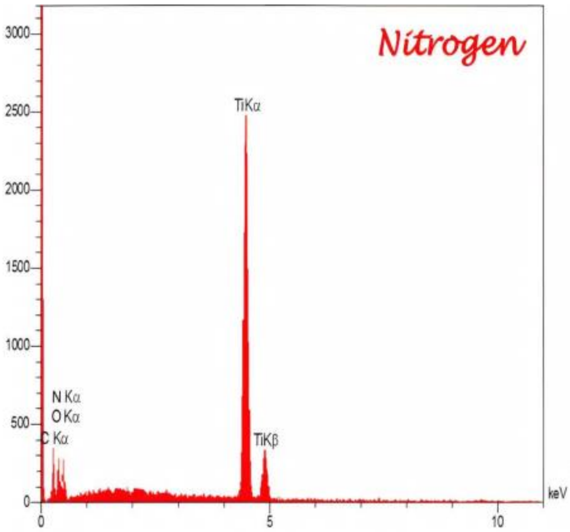
A hydrophilic outer surface with enhanced surface wettability is essential for a material to promote fast osteointegration [26,27]. In the current study, water contact angles for all the research groups are illustrated in Fig. (5) and table (3). As seen from these results, the PEKK coated specimens had lower water contact angle than group C. The PEKK polymer could be the reason for this decrease in the contact angle, which increased the surface roughness and subsequently reduced the contact angle [28,29].



Group C



Group Ar



Group N

Fig. (4) EDX analysis of groups control, argon and nitrogen

Table (3) Descriptive statistic of water contact angle tests

	N	Mean	Std. Deviation	Std. Error
Group C	5	67.6400	1.12827	0.50458
Group Ar	5	34.0400	1.25020	0.55911
Group N	5	34.9400	1.09225	0.48847

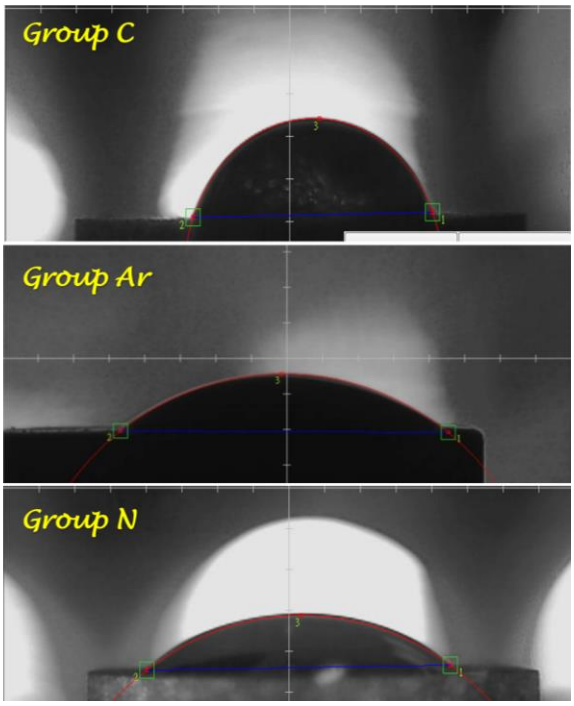


Fig. (5) Images of water contact angle of the study groups

In table (4), the ANOVA test demonstrated a significant difference among all test groups (P<0.05). In addition, A Bonferroni test was employed to compare the mean of group C with the Ar and N groups, which was statistically significant (P<0.05), as shown in table (5). The cross-linking of the PEKK that occurred during sputtering coating technique may explain these results. The cross-linking of the polymer may have altered the surface wettability and increased its hydrophilicity, as demonstrated by Laurens et al. (2000) and Riveiro et al. (2012) [28,29]. Additionally, the surface's ability to attract water increased as the surface roughness increased, leading to an increase in effective surface area. By making the surface rougher, a hydrophobic surface becomes hydrophilic, while a hydrophilic surface becomes even more hydrophilic. This may be in consistent with Wenzel's hypothesis [30,31].

Table (4) ANOVA test of water contact angle

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3665.100	2	1832.550	1364.520	0.000
Within Groups	16.116	12	1.343		
Total	**3681.216**	**14**			

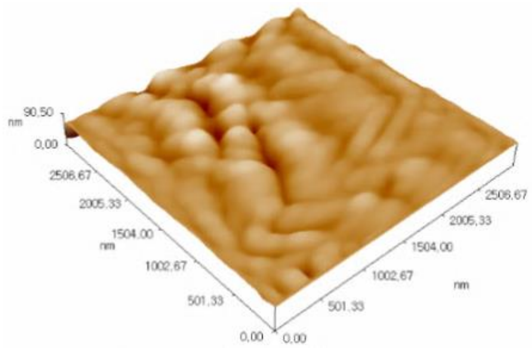
These results may be in agreement with the investigation of Duske et al. (2012), who utilized a cold atmospheric pressure gas-discharge plasma to decrease the water contact angles on Ti disks with a variety of surface topographies. The contact angles of the disks were substantially lowered, approaching zero, regardless of the surface topography, after being exposed to argon plasma with a 1.0% oxygen admixture for either 60 s or 120 s [32].

Table (5) Bonferroni test of water contact angle between groups

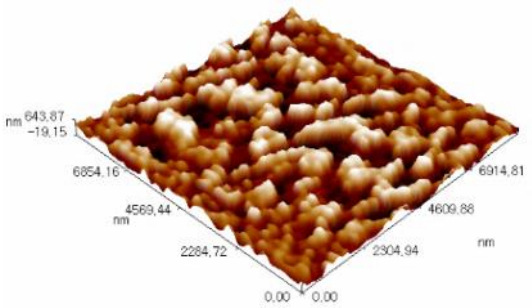
	Mean Difference (I-J)	Std. Error	Sig.
Group C and Group Ar	33.60000*	0.73294	0.000
Group C and Group N	32.70000*	0.73294	0.000
Group Ar and Group N	-0.90000	0.73294	0.729

In relation to implant surface roughness, an increase in roughness enables mechanical engagement with both soft and hard tissues [33]. Implants must be rough for proper bonding to occur with the bone, which in turn enhances osseointegration and improves the overall success rate of implant therapies [34,35].

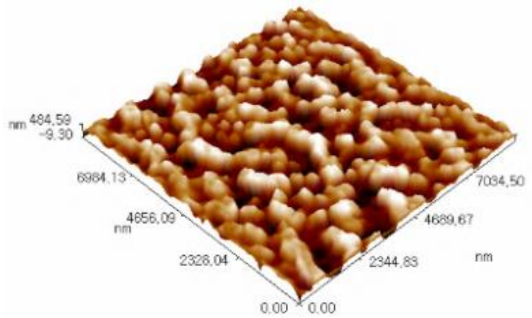
Regarding to this research, the average surface roughness of the group Ar and group N was significantly five times greater than that of the group C (table 6). Figure (6) presents the 3D images for the surface roughness of all tested groups. The ANOVA test showed significant differences across all experiment groups (P<0.05), as shown in table (7). In the Bonferroni test, the results demonstrated a significant variance (P<0.05), as illustrated in table (8), although there is no statistically significant variance (P>0.05) between the Ar and N test groups. This increase in surface roughness was attributed to the PEKK powder, which was beneficial for bone tissue bonding. This observation aligns with the results reported by Rong et al. (2009) and Eom et al. (2012), which demonstrated a notable increase in surface roughness when a coating composed of nano- or microparticles was applied [36,37]. Implants with rough surfaces have been shown to have consistently high and long-lasting effectiveness in clinical studies [38-40].



Group C



Group Ar



Group N

Fig. (6) 3D AFM images of groups control, argon and nitrogen

Table (6) Descriptive statistic of surface roughness test (μm)

	N	Mean	Std. Deviation	Std. Error
Group C	5	0.0274	0.00391	0.00175
Group Ar	5	0.1420	0.01924	0.00860
Group N	5	0.1360	0.01517	0.00678

Table (7) ANOVA test for surface roughness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.042	2	0.021	101.427	0.000
Within Groups	0.002	12	0.000		
Total	**0.044**	**14**			

Table (8) Bonferroni test of surface roughness between groups

	Mean Difference (I-J)	Std. Error	Sig.
Group C and Group Ar	-0.11460*	0.00906	0.000
Group C and Group N	-0.10860*	0.00906	0.000
Group Ar and Group N	0.00600	0.00906	1.000

The XRD patterns for the group C and the groups coated with PEKK are shown in Fig. (7). The XRD pattern of CP Ti specimen had the diffraction peaks at 35.15°, 38.35°, 40.20°, 52.80°, 62.95°, 70.30°, 74.15°, 76.20° and 77.35°. No phase alteration had happened in the CP Ti after PEKK coating. The XRD patterns of the groups were indexed with corresponding international center for diffraction data (ICDD) files (2012). The XRD pattern of the group C showed the peaks of Ti, while the XRD patterns of disk group Ar and group N had identical patterns of the previous literature by Garcia-Leiner et al. (2015) and Alkafaji and Hamad (2020) and Alkafaji et al. (2024) in which they worked on the PEKK [5,41,42]. The XRD patterns exhibit distinct peaks, suggesting that the PEKK in the coats is predominantly semi-crystalline. However, the wide peaks indicate reduced levels of crystallinity, as seen in Fig. (6). This observation aligns with Gruene's findings [43]. This *in-vitro* study found evidence to support the alternative hypothesis and disprove the null hypothesis.

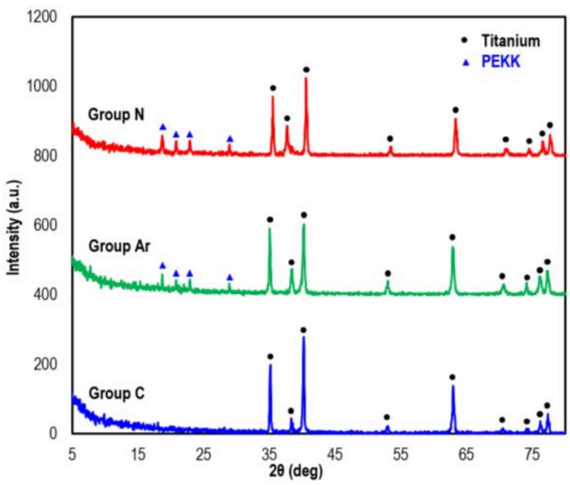


Fig. (7) XRD patterns of groups control, argon and nitrogen

4. Conclusion

The Ti dental implant coating process accomplished by magnetron sputtering did not alter the PEKK phase, provided good adhesion and connectivity, appropriate coat thickness, and improved roughness and wettability. Moreover, both gases are highly recommended in RF magnetron sputtering to apply a layer of PEKK for Ti implant coating. Therefore, this technique of utilizing argon and nitrogen gas in coating led to accelerated bone healing and promoted rapid bone-implant osteointegration.

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