DENTISTRY

Surface Analysis of the PEKK Coating on the CP Ti Implant Using Laser Technique

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ABSTRACT

Objective: **Evaluation of the poly ether keton keton polymer (PEKK) coating material on the commercial pure titanium disks (CP Ti) with or without laser surface structuring.**

Design: **In vitro experimental study of PEKK polymer coated material on the CP Ti disks with or without laser surface structuring.**

Materials and methods: **coating the surface of the commercial pure titanium (CP Ti) disks with PEKK polymer was performed via using frictional mode CO_2 laser, then the samples disks analyzed by using FESEM.**

Results: **the FESEM reveal good adherence and distribution of the PEKK coated material over the CP Ti substrate by using the frictional mode CO_2 laser at 2 watt and 6 ms pulse duration.**

Conclusion: **the frictional mode CO_2 laser considered an effective and suitable method for PEKK coating on the CP Ti substrate.**

KEY WORDS

commercial pure titanium, PEKK polymer, laser, laser surface structuring

INTRODUCTION

The titanium and its alloy can be considered as "gold standard" material for endosseous dental implants between all the available dental implant materials, they position distinguished due to its many desirable properties beside their long-term clinical survival rates for several decades. The titanium and its alloys able to interact closely with the tissue bone beside its highly biocompatible (spontaneous build-up of an inert and stable oxide surface layer)[1)].

The usage of Ti and its alloys as dental implants may be correlated with some disadvantages despite the well evidenced of its usage like, the elastic moduli difference between the titanium implant and the surrounding bone, which led to stress in the bone-implant interface and periimplant bone loss[2)], its dark grayish color[3)] and hypersensitivity to titanium[4)]. Those limitation of the titanium and its alloy coupled with the patients demanding for dental implants metal-free led to using the dental implants made from ceramic and polymer[1,3,5)]; but unfortunately, due to high young`s modulus of the ceramic led to preferring using of polymer[6)].

The dental implants surface modification, specifically the topographical, considered as an effective method for improving bioactivity of dental implants[7)]. Implant rough surface could be provided by utilizing laser that improve the osseointegration. Several studies showed that the implant surface modification by the laser technique can reduce the dental implants contamination with implants torque removal increasing after their implantation in rabbit tibia and femur[8-10)]. The laser surface modification techniques could offer better osseointegration due to formation of surface microstructures with significantly hardness enhancement, corrosion resistance, standard roughness, a high degree of purity and increasing of the oxide layer[11)]. **Bereznai *et al*.** stated that the oxide layer increases extra than doubles after implant surface laser treatment[12)].

The high-performance polymers had better properties than commodity plastics. The group of high-performance polymers who had utilized in the dental field was called poly aryl ether ketones (PAEK). The PEAKs had pulled so much attention because of the feasibility of utilizing them as a substituted to metal in a wider range of applications such as removable dentures and implanted prostheses beside it's used as provisional implant abutment[13,14)]. The PEKK chemical structure was the best mechanical properties of all PAEK family. The compression strength of the PEKK was up to 80% greater than PEEK[15)].

PEKK polymer is a biocompatible material from the PAEK family like PEEK. It's used in medical implants field due to its biocompatibility beside its high mechanical strength; PEKK have high strength, high rigidity, high resistance to hydrolysis, and suitable for extremely demanding conditions. When thermoplastics are processed the chemical properties not change and just its form that is altered. The PEKK also does not shown any porosity or monomers[16,17)].

MATERIALS AND METHODS

Samples Preparation

Circular disks (7 mm diameter and 2 mm thickness) of CP Ti grade (II) (Orotig Srl EU Company, Italy) were cut with wire cut machine (Knuth Smart DEM-Germany), then those disks were bringing to a mirror smooth uniform appearance via rotation machine with Sic Papers proceeded from 500 to 2400 grit. For removing the contamination and

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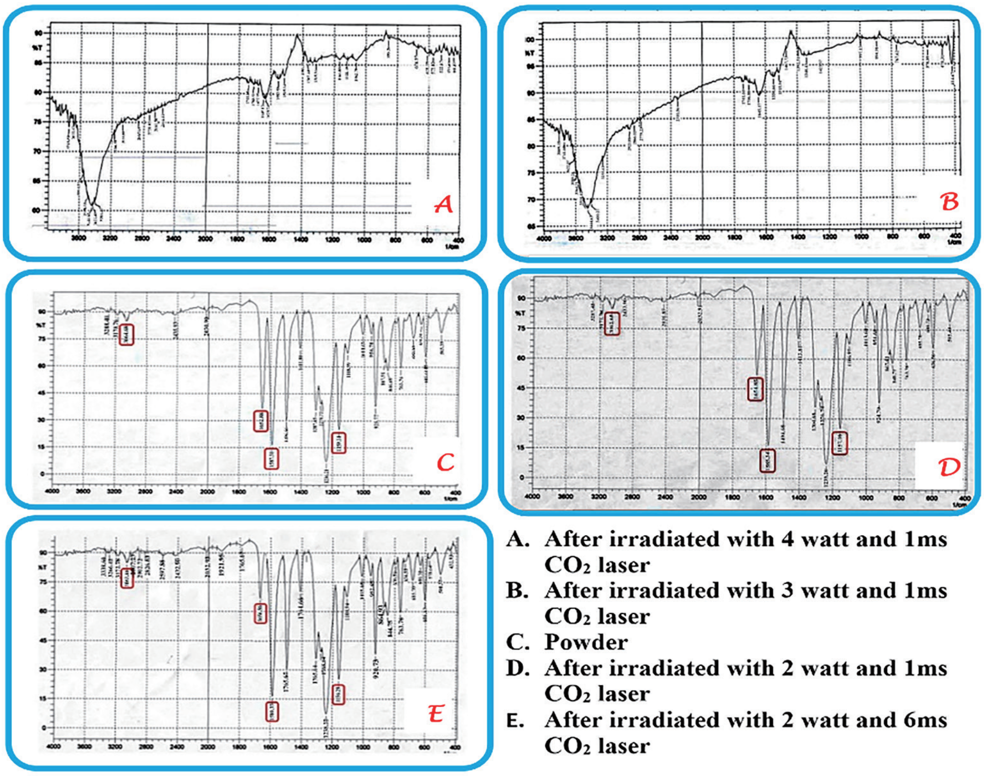
Table 1: The water contact angle of PEKK coating with different duration time of CO_2 laser

Laser pulse duration time	1	2	3	4	5	6	7	8	9	10
Degree of water contact angle (o)	38.73	34.28	30.72	24. 15	22	20.04	25.89	34.55	43.63	48



A. After irradiated with 4 watt and 1ms CO_2 laser
B. After irradiated with 3 watt and 1ms CO_2 laser
C. Powder
D. After irradiated with 2 watt and 1ms CO_2 laser
E. After irradiated with 2 watt and 6ms CO_2 laser

Figure 1: FTIR Spectrum of PEKK

the debris the samples were putted in the ultrasonic cleaning device for (15 minutes with ethanol) then for (10 minutes with distilled water) respectively. Finally, the samples were dried at room temperature for 15 minutes[18].

Surface Structuring by Laser

The laser system performed the desired profile on the titanium disk surface. The surfaces of the CP Ti were structuring under normal atmosphere by using pulse mode CNC fiber laser machine (Jinan JinQiang 20W laser– China) with laser power 20-Watt, wavelength 1064 nm, and scanning speed up to 7000 mm/sec. The design that used for structuring the samples was the dot design over the whole surface of the sample with 0.01 mm space between each adjacent dot in all directions. Corel Draw software (version XII) was used for drawing the dot design shapes. The samples-laser source disk distance was 20 cm. When the system triggered on, the sample was starts shooting by the laser with a continuous series of laser pulses in an ablation process to form the dot design[18].

Laser Coating Technique

Approximately 1 g of PEKK polymer powder (GAPEKKTM, 3200P, Gharda chemicals. India) was dispersed in 100 ml of distilled water that contain 3g of para chlorophenol (HiMEDIA, India) that used to gain a homogenous slurry (The para chlorophenol was suitable solvent solution for solvent the PEKK), which was preplaced as a powder bed on the surface of the CP Ti; the substrate was spray-coated with the slurry[9,18], thin layer of PEKK powder was preplaced on the CP Ti substrate when the solvent was evaporated.

A frictional mode CO_2 laser (I2itek, Fractional, HQ Dublin, Ireland) was used for coating the PEKK on the CP Ti samples at 10.6 µm wavelength, 0.1 mm spot diameter and 0.1 mm distance between each adjacent exposed spot (So laser was completely exposed to all regions of the PEEK); the disk to lens distance was 5 cm. Numerous trials were carried out for achievement appropriate laser coating parameters for best coat layer.

During coating procedure all the laser parameter was fixed while the CO_2 laser power was only the parameter that change, three different laser powers was examined for the PEKK coatings, which are 2, 3 and 4 Watt. the PEKK coated layer were examined visually and then by FTIR (Biotech, FTIR-600, UK) to be sure that the CO_2 laser does not cause any damage effect or decomposition to the PEKK.

The visual results of using CO_2 laser PEKK coated shown that, the PEKK coated layer become brown in color when exposed to (3 and 4) watt power this means that damage was happened to the PEKK polymer, the damage effect was confirmed by the FTIR spectrum Figure 1(A and B) that revealed the main bands of the PEKK polymer was not found when compared with the spectrum of the PEKK powder figure 1 (C), {The main bands groups of PEKK molecule are (C = H) benzene ring which have 3064 Cm^{-1} absorption bands, ketone(C = O) which have 1652 Cm^{-1} absorption bands, (C = C) aromatic ring which have 1587 Cm^{-1} absorption bands, and (C-O) ether bond which have 1159 Cm^{-1} absorption bands}. While the results of CO_2 laser PEKK coated at 2 watt shown that the PEKK coated layer remain white in color, the FTIR spectrum of the PEKK coated layer that exposed to 2 watt figure 1(D) shown the present of the main bands of the PEKK; so this means that the 2 watt power with 1 ms pulse duration of CO_2 laser not caused any decomposition or any structural chemical changes to the PEKK polymer.

Ten duration time from (1 to 10) ms were used for selection the best duration time of PEKK coating by using 2 watt CO_2 laser. Since the wetting properties is very important in implantable material and considered as indicator for future good osseointegration, so surface wettability test (water contact angle test) was used to measure the amount of the PEKK coated layer wettability for the ten tested duration times (1-10) ms. The disk with low contact angle measurement (high wetting surface) was chosen for PEKK coating of the final CP Ti samples. Table 1 shown the degree of water disk contact angle for each laser duration time (1-10) ms at 2 watt CO_2 laser.

The results of the water contact angle test shown that the PEKK coating by the CO_2 laser at 2 watt with 6 ms duration time gives the best

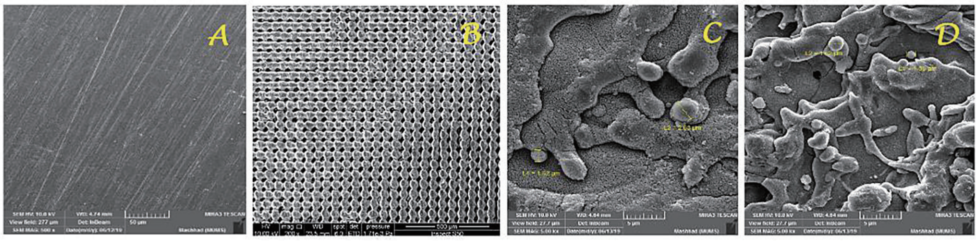


Figure 2: FESEM analysis of A) control, B) LS group, C) P group, D) LS-P group

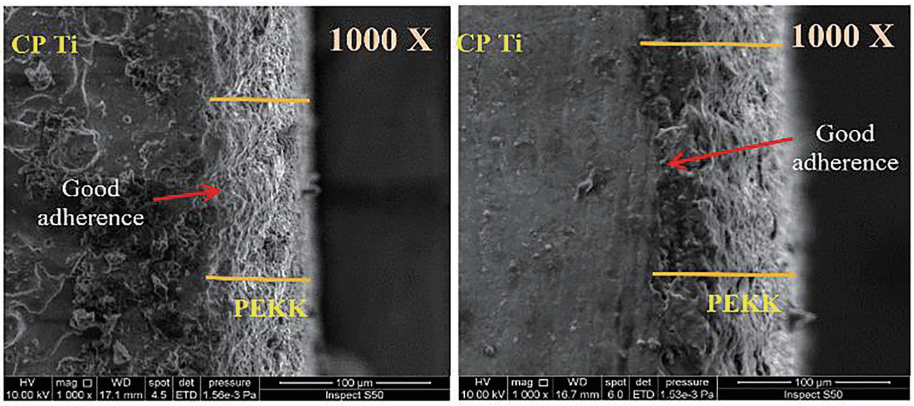


Figure 3: The cross-section images of the FESEM, group P left images, group LS-P the right images

hydrophilicity of the PEKK polymer (the low value of water contact angle).

The FTIR spectrum was performed at 6 ms duration time to be sure it was safe to use for PEKK coating. The main groups of the PEKK polymer were found in the FTIR Figure 1(E). So, no damaging effect to the PEKK was occurred. Therefore, the laser coating technique was performed by using CO_2 laser (fractional mode) at 2 watt power, 6 ms pulse duration, 10.6 µm wavelength for the final CP Ti disks coating with PEKK polymer. Lastly the top surface of the samples of all groups was analyzed by FESEM.

Samples Grouping

The CP Ti disks were divided into four groups which are:

1. **The control group (C):** CP Ti disk without any laser surface structuring and coating.
2. **Laser surface structuring group (LS):** CP Ti disk with laser structuring.
3. **PEKK coating group (P):** CP Ti disk with PEKK coating
4. **Laser surface structuring with PEKK coating group (LS-P):** CP Ti disk with laser structuring and with PEKK coating.

Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscopy (MIRA3 TESCAN, Czech Republic) was used to examine surface morphological topography of the C, LS, P and LS-P groups, PEKK particle size, the PEKK coating thickness and the PEKK adherence to the CP Ti substrate.

RESULTS

Surface Microstructure

The surface morphological analyses of CP Ti samples were seen in Figure 2 (A), the group LS shown in figure 2 (B), while the samples that coated by PEKK polymer groups (P and LS-P) were seen in Figure 2 (C, D) respectively.

Particles Size Analysis

The coated PEKK particles size was investigated by using FESEM, the particles size was ranged from (1-3) µm for the groups P and LS-P as seen in Figure 2 (C and D).

PEKK Coating Thickness

From the cross-section images of the FESEM the thickness of the PEKK coating could be obtained figure 3. The thickness of the PEKK coating material for group P was about 31.95 µm as, while the thickness of the PEKK coating material for group LS-P was about 38.6 µm.

PEKK Coat Adherence to the CP Ti Substrate

The cross-section images of the FESEM of the PEKK coated material figure 3 shown nearly uniform distrubuted on the CP Ti substrat with very good adherence in all the coated areas without present of any gaps between them.

DISCUSSION

Surface Microstructure

The FESEM of the group C had shown nearly smooth surface with linear lines that happen due to manufacturing and processing; while for the groups LS, P and LS-P had shown surfaces with roughness and porous like the structure of the bone, which had a beneficial effect to cell adhesion, this result in agreement with **Meng *et al.* in 2016 and Safi in 2019**[19,20].

The images of LS group shown very fine clear and uniform dots structure all over the examined samples with no defect or any inconsistent structures on them, while the images of the PEKK coated layer of the groups P and LS-P displayed homogenous continuous surface, which means that PEKK evenly and uniformly scattered on the CP Ti with, this uniform distribution layer of PEKK was possibly due to the technique that used during coating by utilizing homogenous slurry of the PEKK with para chlorophenol during the coated layer on the surface of the substrate, in addition to the using of CO_2 laser with proper parameters for PEKK coating that helped in proper distribution of the coated layer, this comes in agreement with **Malek *et al.*; Goodarzi, and Safi**[20-22].

PEKK Coating Thickness

The average PEKK coating thickness for group LS-P was greater than the group P; this may be due to the effect of the surface structuring that increase in roughness which may lead to inflowing of the PEKK to the pits that gives this thickness.

PEKK Coat Adherence to the CP Ti Substrate

The cross-section images of the FESEM shown good adhesion of the PEKK coat layer on the CP Ti substrate with and without laser surface structuring and absent of any gaps between them. this result was similar to the results of **Gary *et al*. in 2005; Shivamurthy *et al*. in 2008, Safi in 2019 and Al-Khafaji in 2020**[16,20,23,24]; whose used the cross section image of FESEM to seen the adherence of the coated material with the substrate.

SUMMARY

Coating of the CP Ti substrate with PEKK by using CO_2 laser method can be produced coating with uniformed distribution and excellent bonding to the CP Ti substrate (with and without laser surface structuring).

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