

Biocompatible Coating of Polyetheretherketone Biomaterials and Its Characterization

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Abstract

Polyetheretherketone (PEEK) is a semi-crystalline synthetic thermoplastic polymer that has excellent mechanical properties, elastic modulus similar to bone, chemical stability and good biocompatibility. However, PEEK has a bio-inert surface and because of that it does not interact enough with host environment. One of the best methods to solve this problem and improve the surface properties of PEEK is surface coating with bioactive materials. The aim of this study is coating PEEK substrates with Titanium (Ti) and Hydroxyapatite (HA) using Atmospheric Plasma Spraying (APS) and characterization coated PEEK biomaterials. Structural characterization performed by Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD). Roughness measurements and micro hardness tests were performed in order to mechanical characterization. The results showed that biocompatibility of PEEK biomaterials can be improved with the Ti/HA multilayer coatings.

Key words: Polyetheretherketone , Titanium, Hydroxyapatite, Atmospheric Plasma Spray

1. Introduction

Metallic implants such as Titanium (Ti) and its alloys, stainless steels and Cobalt-Chromium alloy are one of the most known materials in orthopedic and dental applications because of their biocompatibility, corrosion resistance and superior mechanical behaviors[1,3]. However metallic implants have some disadvantages such as wear, stress shielding, ion leakage in long term usage and elastic modulus mismatch with human bone [1-4].

Polyetheretherketone (PEEK) is a semi-crystalline high-performance thermoplastic polymer which emerged in the late 1990s, with outstanding mechanical properties, good chemical stability and good biocompatibility. PEEK has a melting temperature of 343 °C which offers high thermal stability up to 260°C [4-6]. PEEK also is a radio-opaque biomaterial which is an important advantage for imaging systems such as computed tomography (CT) and magnetic resonance imaging (MRI) [7]. But most importantly PEEK has a good sterilization capacity [8] and an elastic modulus which is similar to natural human bone. These superior properties of PEEK make it a suitable biomaterial for trauma, orthopedics and spine implants [5]. Also industrial grade PEEK polymers have been widely used in aircrafts, turbine blades and oil refinery pipes [5, 9, and 10]. But , the bio-inert behavior of PEEK pose an obstacle to the generating of a chemical bond with human bone tissue, and because of that reason formation of that bond can be delayed or the resulting bond can be weak [2]. If this problem can be fixed, then PEEK will be a superior polymeric implant which can replace the metallic implants such as Ti and its alloys.

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In this regard, improving the PEEK implant materials bioactivity is an important problem that must be solved to fully reveal of PEEK biomaterials potential. Recently, two main strategies have been widely used to enhance the bioactivity of PEEK: one of them is surface modification and the other one is composite preparation [5]. One of the best ways of surface modification is coating the PEEK implants surface with a bioactive material such as Titanium (Ti) and Hydroxyapatite (HA). Because of its very protective oxide layer and excellent bioactivity, Ti is one of the well-known metals which have been used in producing metal implants. The natural TiO₂ layer protects itself and during any damage or failure it can be reformed immediately [5,11 and 12]. Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), is known with its similarity to the natural bone. Because of that HA can promote to the formation of natural bone via its calcium and phosphate ions, HA have been accepted as one of the best bioactive materials. Still, its mechanical properties prevents the use of HA as bulk material. Thus using HA or its combinations as a coating material gives the advantage of good bioactivity and desirable mechanical properties [13-15].

Due to PEEK biomaterials low melting temperature, only a few surface coating methods can be used for depositing bioactive materials such as Ti and HA without degrading the substrate material. Cook et al. [16] used plasma vapor deposition (PVD) to coat Ti onto PEEK substrates, Devine et al. [17] coated carbon-fiber reinforced PEEK biomaterials with Ti via physical vapor deposition (PVD) and vacuum plasma spraying (VPS) and Beauvais et al. [18] coated PEEK and Ti-6Al-4V substrates with HA using atmospheric plasma spray (APS).

The objectives of this study were coating PEEK substrates with Ti and HA bioactive materials using Atmospheric Plasma Spray (APS) coating technique and structural characterization of coated products.

2. Materials and Method

Commercially available PEEK samples were used as substrate for coating process. PEEK samples grit-blasted with a medical grade alumina (Al₂O₃). After grit blasting procedure, the samples cleaned with distilled water by using ultrasound to remove any remaining blasting material.

Bilayered Ti coated PEEK samples coated with HA in order to obtain a multi layered coating. The aim of the coating production was investigation of coating deposition behavior on PEEK substrates. An Atmospheric Plasma Spray (APS) system consisting of 6 axis robot arm with a F4-MB plasma gun (Oerlikon Metco, Formerly Sulzer Metco, Switzerland) was utilized to produce the coating system. Traverse speed was set to 300 mm/s for producing all coating layers and plasma spraying parameters for Ti and HA are given in Table 1. During the coating operation Argon used as the main plasma gas and 5 passes of spraying were conducted. After 5 passes coating operation was stopped. Medical grade HA powders with an average diameter of 30 µm were fed into spraying gun. The size distribution of HA powders are given in Figure 1.

Table 1. Coating parameters of Atmospheric Plasma Spray

Coating Powder	Argon Flow (NLPM)	Hydrogen Flow (NLPM)	Current (Ampere)	Carrier Gas (NLPM)	Disk Speed	Spray Distance (mm)	Traverse Speed (mm/s)
Titanium	70	0M	540	3.5	12%	200	300
Hydroxyapatite	70	8	540	3.5	12%	200	300

As-sprayed coating samples were sectioned and cold mounted in resin at 200 mbar. After that samples grinded and polished for cross-sectional examination. Scanning electron microscopy (TESCAN; Vega SBU II, Czech Republic) was used to examine the Ti/HA coatings through the cross-section on the substrate/coating interface area. Coating thickness, porosity and homogeneity were determined by examination of several areas. The coating chemical compositions were evaluated by using energy dispersive X-ray spectroscopy (EDX).

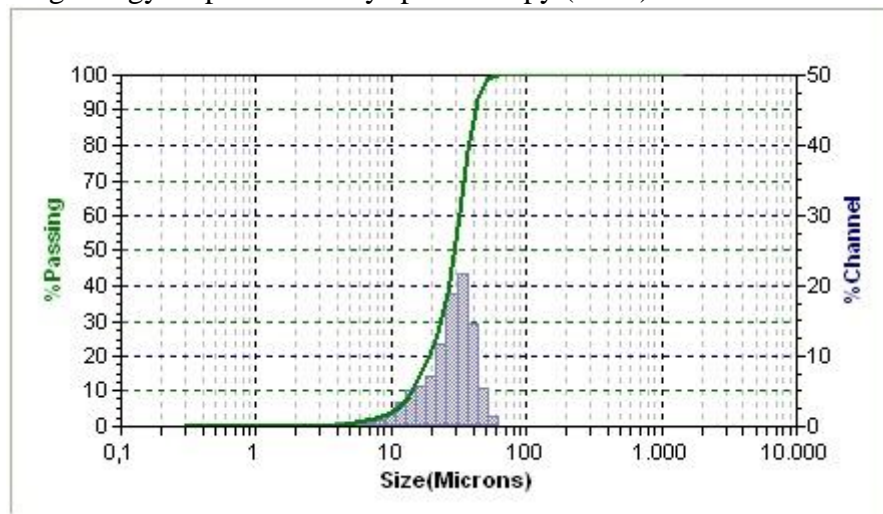


Figure 1. HA powder size distribution

XRD analysis were performed by PANalytical Empyrean X-Ray diffractometer with a Cu $K\alpha$ radiation on the surface area of sprayed HA and uncoated section of PEEK substrate with a 2theta scanning range of 20 to 60 degrees. Roughness measurements performed by Mitatoya SurfTest SJ-301 Profilometer on the HA coated surface and uncoated surface area. Micro hardness measurements performed with 50 gr load for 10 seconds by Futuretech Micro Hardness Tester on the uncoated PEEK, Ti coated and HA coated sections.

3. Results

Figure 2.A shows macro image of coated PEEK polymer, and Figure 2. B and C show back scattered electron (BSE) views of SEM. SEM images reveal that overall coating structure which consists as, at the bottom PEEK substrate, Ti coating as bright section on top of PEEK polymer and HA coating on the top of Ti coating as gray section.

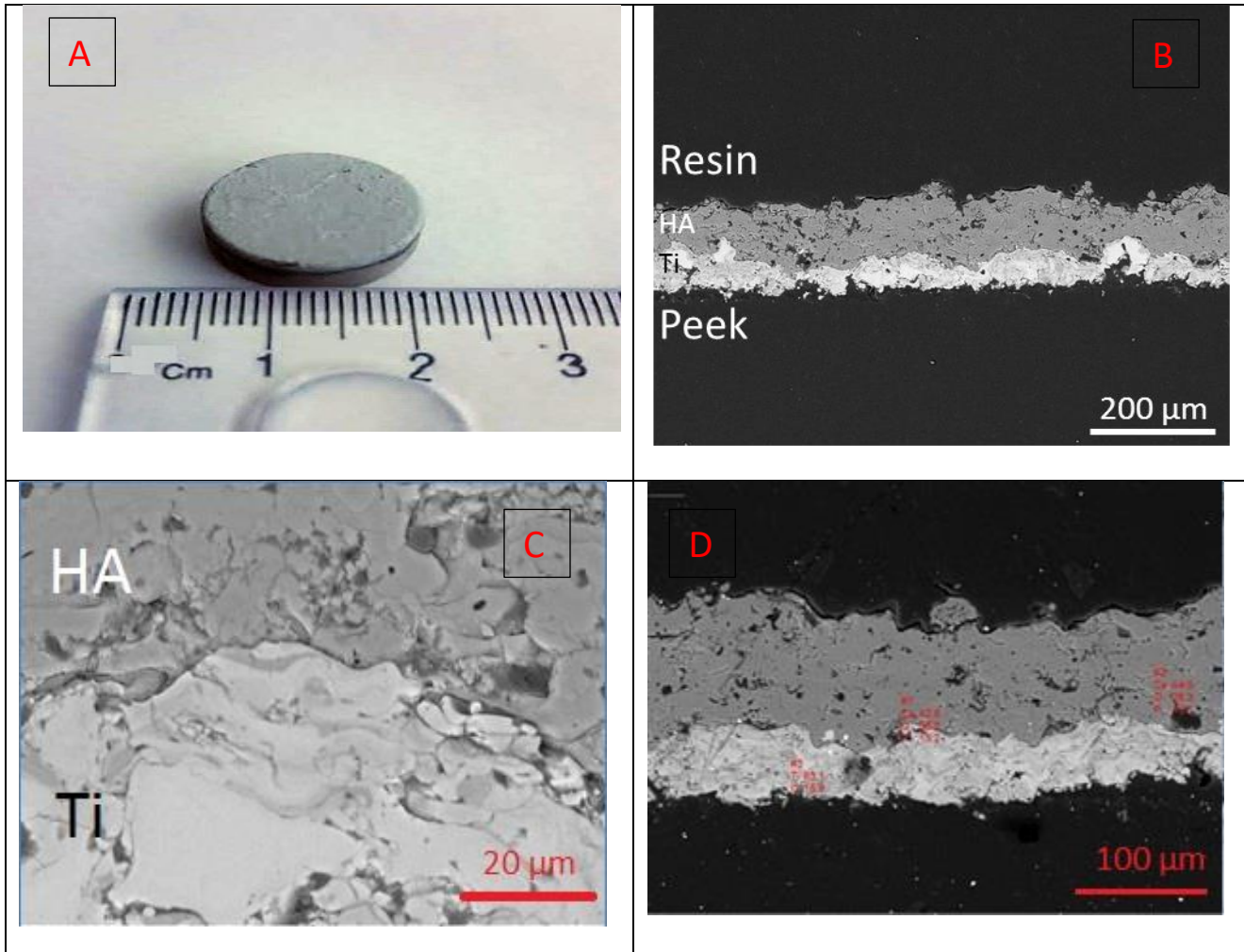


Figure 2. A) Macro image of coated PEEK polymer, **B and C)** BSE – SEM images of Ti/HA coated PEEK implants with a respectively magnitude of growth rate 250X and 2500X. **D)** Chemical composition analysis of Ti and HA coatings.

Coating thickness measurements performed in BSE images of SEM. As can be seen in Figure 2.B average coating thickness of Ti coating layer is 44, 52 μm and average coating thickness of HA layer is 114, 41 μm . For deposition efficiency calculation, average coating thickness divided to total spraying passes. Therefore, deposition efficiency for HA coating is higher than titanium deposition.

It can be seen from Figure 2. B and C, there is a porous surface structure at the top of the HA coating. Roughness measurements showed that while average roughness value (R_a) for uncoated PEEK is 2, 57 μm and the maximum roughness height (R_y) is 22, 94 μm , for the Ti/HA coated specimen R_a is 8, 07 μm and the (R_y) is 61, 93 μm .

XRD analysis performed in order to reveal crystal structure of HA coated layer and PEEK substrate. Figure 3 shows the XRD spectrum of sprayed HA layer. Peaks at 25.8, 31.8, 32.1 and 32.9 degrees that corresponds to reflections (002), (121), (112) and (300) are evidences for the presence of HA phase.

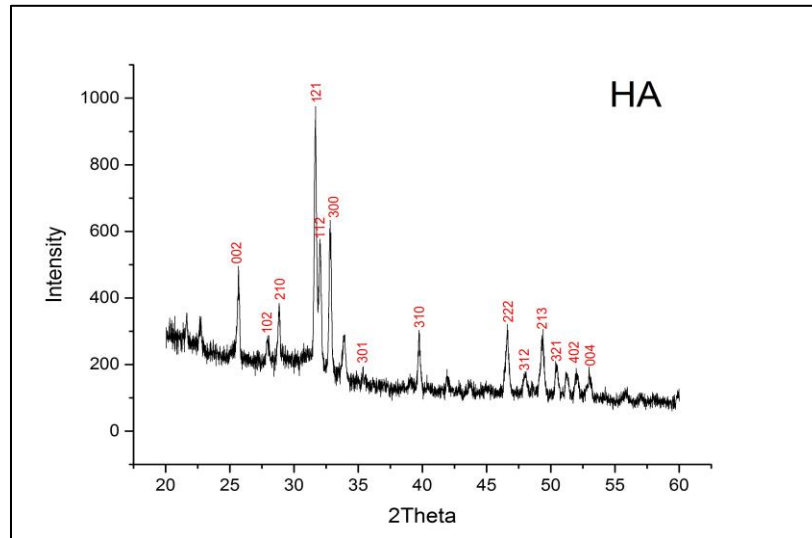


Figure 3. XRD spectrum of HA coated layer.

In Figure 4. an XRD spectrum of PEEK substrate is given. In the XRD spectrum peaks which indicate semi-crystal structure of PEEK can be seen clearly.

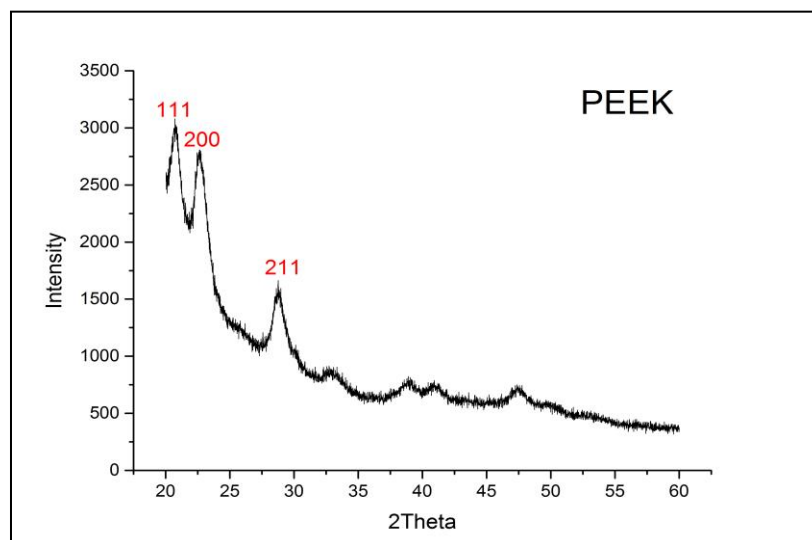


Figure 4. XRD spectrum of PEEK substrate.

An average micro hardness value of 22, 4 HV_{0.05} obtained for PEEK substrate. Average hardness value of Ti coated layer is 527, 06 4 HV_{0.05} and average hardness value of HA coated layer is 194.6 4 HV_{0.05}.

4. Discussions

As can be seen in Figure 2.C melted Ti droplets deposited onto the PEEK substrate successfully. Coating cross-section analyses at the interface shows that a good interlocking between Ti and PEEK. It can be seen that there is no crack or void formation between Ti coating layer and PEEK substrate which indicates that the process did not damaged PEEK substrate. The good quality of interface between Ti coating and PEEK substrate is an evidence of good adhesion strength. At the interface between Ti coating and HA coating good interlocking can be seen same as between Ti coating and PEEK substrate. Interface between sprayed titanium and HA shows good adhesion as it can be seen in Figure 2. C.

Total average coating thickness obtained with APS deposition technique in our study measured as 158.93 μm . Beauvais et al. [18] deposited HA onto PEEK by vacuum plasma spraying (VPS) and obtained an average coating thickness of 158 μm . Walsh et al. [19] coated cylindrical PEEK dowels coated with Ti by using vacuum plasma spray and an average coating thickness of 200 μm was obtained. It can be seen that coating thickness that obtained in our study, supports the thickness measurements of other studies in the literature.

Chemical compositions of coatings were determined by EDX analysis. As can be seen in Figure 2.D, in order to obtain coating composition several measurements evaluated. The results of chemical composition of coatings show that, in the Ti coated layer existence of Ti and O elements is proven. Titanium oxide during spraying is inevitable despite the use of argon because of high temperature nature of plasma spraying. Because of the APS coating characteristics and oxide forming tendency of titanium, Ti coated layer consists titanium and oxide formations which is an advantage for improving the biocompatibility. In the HA coated section, existence of Ca, O and P is proven which indicates of HA formation.

As mentioned in results section, in our study surface roughness increased after the deposition. Devine et al. [17] coated carbon-fiber reinforced PEEK screws with Ti by using VPS and PVD, and used them in animal models. Devine et al.[17] stated that torque removal and bone contact area measurements of PVD and VPS coated screws showed that VPS coated screws has better torque removal and bone contact area values which is considered as the result of surface roughness. Several studies reported that implants with a rough surface have better stability of implants, increases the amount of the blood cells and supports formation of bone tissue [20-23]. Thus with the increasing roughness values of PEEK implants, biocompatibility can be increased too.

XRD result revealed that coating surface consists from HA phase. Crystallinity of HA is an important aspect to obtain desired mechanical properties. Also in order to increase bone growth rate one of the most important properties is crystalline of HA [24, 25]. It can be seen in Figure 3 that HA has a well crystallized structure. On the other hand, crystallinity degree of PEEK polymers is an important specialty to obtain better mechanical properties such as yield strength, toughness and elastic modulus. In Figure 4 XRD spectrum peaks which indicate semi-crystal structure of PEEK can be seen clearly. XRD analysis of PEEK substrate also reveals that there is no degradation in the structure of PEEK which is caused by high process temperature during coating operation.

Hardness measurements revealed that the hardest phase of the coated product is Ti layer. Also, after the deposition overall surface hardness value of the implant material increased. It is known that with the increasing hardness, a better wear resistance can be obtained. Hardness measurements indicate that coated PEEK polymeric implants are likely to have a better wear resistance which is an essential property for implant usage life.

Conclusions

PEEK polymeric biomaterials successfully coated with titanium and hydroxyapatite using atmospheric plasma spray. Scanning electron microscope images revealed good binding between substrate and sprayed Ti layer interface. Sprayed Ti and HA layers also showed good adhesion without any voids and crack formations as well. According to thickness measurements deposition efficiency of titanium was found lower compared to HA layer. Chemical composition analysis revealed the formation of hydroxyapatite and titanium oxide which increases the biocompatibility of PEEK implants. Roughness values of Ti/HA coated PEEK samples indicate a better blood cell growth rate and bone tissue formation compared to uncoated PEEK. XRD analysis revealed that crystalline HA structure obtained with the coating operation. It is also seen in the XRD analyses; PEEK preserves its semi-crystal structure and shows no degradation. Finally hardness measurements showed that coated samples have a better hardness value which helps to increase the wear resistance of implant material.

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