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Plasma Sprayed Biocompatible Coatings on PEEK Implants

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Abstract

New advanced polymeric biomaterials such as implantable poly(etheretherketone) (PEEK) are changing the face of the implantable medical device industry. Due to its bioactive behavior in vivo, hydroxyapatite (HA) coatings are used to improve the bone growth and to repair around metallic implant. The objective of this work is to study the feasibility of plasma sprayed hydroxyapatite coating on PEEK material.
Different PEEK (unfilled and composite) specimens were successfully coated with a 150 µm thick coating. Chemical and crystallographic compositions, adhesions and microstructures of HA coatings on PEEK and on Ti-6Al-4V were compared. The results showed that the structure of HA coatings were appreciably equivalent. Mechanical tests showed that the plasma spraying process did not severely degrade the initial properties of the PEEK substrate.

Introduction

Introduced in an implantable grade in 1999, PEEK-OPTIMA® has been already used for orthopedic and dental implants, cleared by FDA and CE marked. Indeed, PEEK presents many advantages: it is non magnetic (enables MRI scans), biocompatible and a high mechanical performance material for medical devices. Moreover, contrary to metal implants, PEEK implants do not produce a shadow which masks the tissue and bone growth and repair during the X-Ray post-implant inspection. Furthermore, PEEK's modulus and density are closer than metal values to the natural bone (PEEK: 4 GPa, 1.3 $g.cm^{-3}$; Bone: ~ 10 GPa, ~ 1.5 $g.cm^{-3}$; Ti alloy Ti-6Al-4V: typically range from 80 to 125 GPa, 4.6 $g.cm^{-3}$). Moreover, PEEK can be carbon fiber-reinforced in order to obtain a very promising anisotropic implant material since the structure of bone is highly anisotropic.

Surface compatibility between tissue and implant surface can be enhanced by coating the implant with a bioactive material such as hydroxyapatite. Plasma-spraying is an established method to coat metallic medical devices with hydroxyapatite.Many studies of plasma sprayed HA coating on metallic substrates have been performed [1-3] but only few studies exist concerning plasma sprayed HA on polymers and composite materials [4, 5]. In this work, preliminary investigations of the influence of the plasma-spraying process on the properties of PEEK (unfilled and carbon fiber-reinforced) are presented.

Materials and Methods

Materials and Process

Existing technology and know-how which are commonly used for metallic implants were used as a basis for the optimization of plasma spraying on PEEK.

Different unfilled PEEK specimens (PEEK-OPTIMA®, Invibio, Thornton Cleveleys, UK) (4 mm thick) were used: 25 mm diameter disks (for adhesion tests), 45x205x4 mm^3 plates (for cross section metallographic observation), 75x45x4 mm^3 plates (for chemical and crystallographic composition measurements), tensile and flex bars 80x25x4 mm^3 (for the mechanical tests) and even demonstrators and prototypes of medical devices with complex shapes (spine cages) (Figs. 1 and 2). Carbon fiber reinforced composite PEEK (CF/PEEK-OPTIMA®, Invibio, Thornton Cleveleys, UK) 25x25x4 mm^3 plates were also coated with the same process. The diameter of the carbon fibers is 7 µm with mean length 200 µm. Using image processing analysis the fiber volume fraction was measured to be 25 %.

PEEK shows different thermal and mechanical properties, compared with metallic substrates. A titanium alloy was chosen in reference: Ti-6Al-4V. Titanium samples were coated in same conditions for comparison.

The specimens were grit-blasted with alumina in order to obtain Ra ~ 5 µm roughness, cleaned with ethanol and dried in an oven at 100°C during 2 hours. As far as plasma spraying is

concerned, an oscillating movement of the plasma torch was optimized to minimize the thermal impact on the substrate.

PEEK, CF/PEEK and Ti-6Al-4V were coated with a spherical spray-dried hydroxyapatite powder (average grain size: 120 µm) using an APS system and an F4MB plasma torch (SULZER METCO, Switzerland).

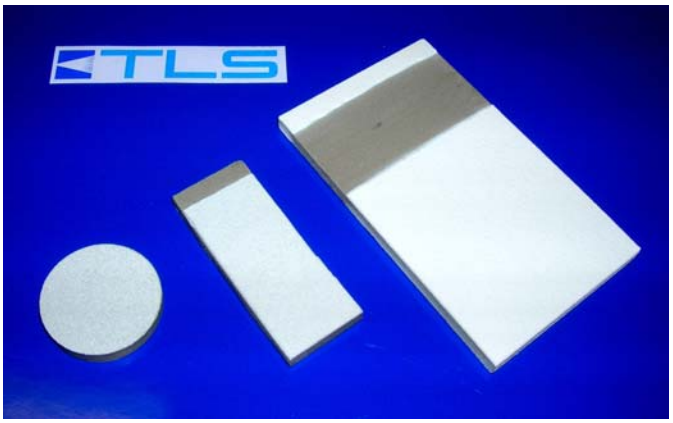


Figure 1: Coated pure PEEK disk (100 µm), and plates (middle: 150 µm; right 500 µm). The grey bands are uncoated surfaces (protected with specific masks during plasma spraying).

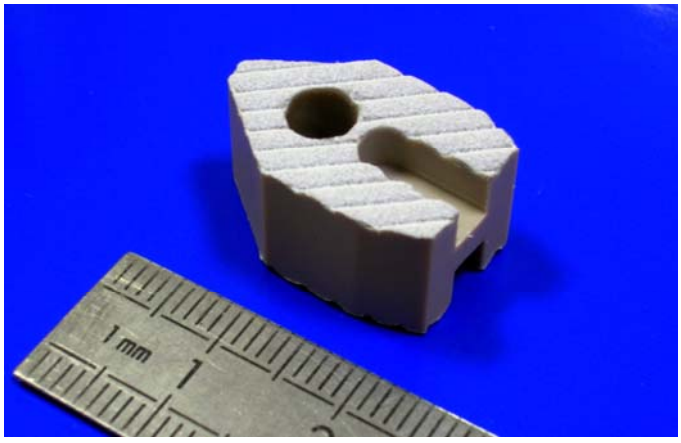


Figure 2: HA coated pure PEEK demonstrator (150 µm).

Temperatures Measurements

Plasma spraying process is based on the melting and spreading of hydroxyapatite particles on grit blasted surface. Coating results from building-up of partly melted droplets. Hydroxyapatite has a melting temperature of 1650°C; PEEK has a glass transition temperature of 143°C and a melting temperature of 343°C. Moreover, PEEK has a very low thermal conductivity (0.25 WmK^{-1}) compared with Ti-6Al-4V (6 WmK^{-1}). In consequence, a particular control of the cooling system is necessary during the spraying step in order to avoid PEEK damage. No physical deterioration of the pure and composite PEEK substrate was observed: no dimension or color variation was detected. Temperatures were measured thanks to a thermocouple placed in a hole 1 mm under the surface and with thermosensitive tickets stuck under the specimen and on the masked areas (with silicone-glass tapes). The temperature increased from 25°C to 70°C and returned to 25°C in less than 2 minutes. The tickets indicated that the maximum temperature surface was between 65°C and 82°C. PEEK can be used up to 260°C. It is therefore assumed that the initial PEEK properties were not degraded.

Coating Surface and Cross-section Analysis

Coated implants were examined by Scanning electron microscopy (SEM, Zeiss Gemini DSM 982) to analyze coating morphology, coating integrity and microcracks. For cross-section analysis, the specimens were cut perpendicular to the coating, embedded in epoxy resin and polished. Optical investigations on cross-section were made to analyze the coating microstructure. Coating thickness and closed porosity rate were measured in an image analysis system (Pegase Pro, 2ISystem, France). Disks, mechanical specimens and implants have coated with a 150 ± 50 µm thick coating. In order to obtain sufficient materials for composition measurements, large plates were coated with a 500 µm thick coating. We can notice that in spite of the high thickness, no delamination was observed. Additional backscattering electron investigations (BSE) were made on cross-section in order to analyze the influence of the pre-treatment by grit-blasting on the interface.

Surface Roughness Characterization

Roughness of the substrate after grit-blasting and of the HA coatings were determined by using a roughness measurement device (Perthometer M2, Mahr, Germany) with a profile length Lt = 17.5 mm (for substrate) and Lt = 5.6 mm (for coating), with a cut-off Lc = 2.5 mm (for substrate) and Lc = 0.8 mm (for coating).

Chemical Characterization

Chemical composition of the 500 µm thick coating was controlled. In reference with the ASTM F1185-03 [6] standard, As, Cd, Hg and Pb concentrations have measured using ICP spectroscopy. The powder feedstock, the coating on PEEK and the coating on Ti-6Al-4V presented the same values in conformity with ASTM (Table 1.).

Crystallographic Characterization

The 500 µm thick coating was pulled off, crushed and sieved between 20 and 40 µm. For Ca/P ratio measurements, the powder was burnt in air at 1000°C during 15 hours. X-ray diffraction of the hydroxyapatite was performed with an X-ray diffractometer (CPS 120, INEL, France) with CoK_α. The data were collected in the 2θ range 0°-180° with a resolution of 0.02°. Ca/P ratios were calculated thanks to the areas of peaks in accordance with standard NF S94.066 [7]. Degree of crystalinity is calculated with the division of areas of the 10

biggest peaks of crushed coated by the areas of the 10 biggest peaks of an ultra-pure hydroxyapatite powder.

Adhesion Testing

To measure the tensile adhesion strength of the HA coating on the PEEK substrate, a testing device was used in accordance with standard ISO13779-4 [8]. The speed is 1 $mm.min^{-1}$. Five PEEK disks were glued on the coating with a polyamide-epoxy adhesive film (FM1000, American Cyanamid Company, USA) cured for 2 hours at 180°C. One additional only grit-blasted PEEK disk was glued in order to determine the glue adhesion strength: 18.2 MPa. Normally, the adhesion strength for this glue is ~ 90 MPa for Ti-6Al-4V substrate.

Mechanical Testing

Both sides of tensile and flex bars were coated in order to verify that the plasma spraying step does not degrade the initial properties of the PEEK. The test methods are listed in Table 3.

Results and Discussion

The chemical and crystallographic composition (Table 1), the adhesion and the microstructure (Table 2) of the HA coatings on pure PEEK were measured and compared with the HA coating on Ti-6Al-4V.

Table 1: Chemical and crystallographic composition of HA sprayed on Ti-6Al-4V and on PEEK.

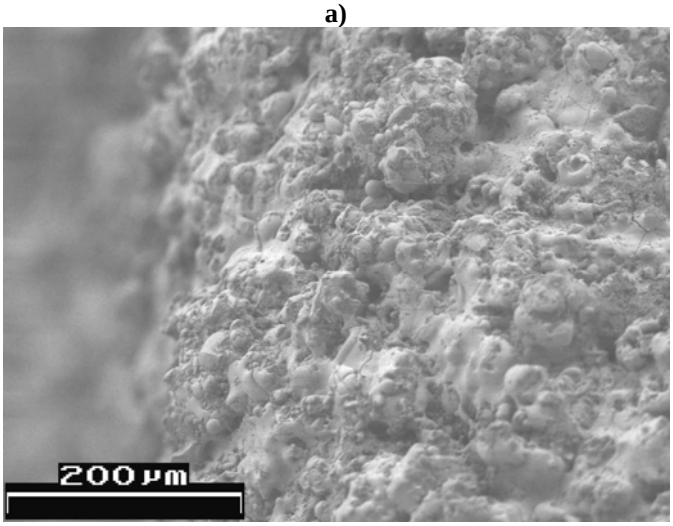
	HA on Ti-6Al-4V	HA on PEEK	Standard
Ca/P	1.695	1.694	NF S94-066
Crystallography:			NF S94-097
α-TCP	≤ 3 %	≤ 3 %	
β-TCP	≤ 3 %	≤ 3 %	
T-TCP	~ 4 %	≤ 3 %	
CaO	≤ 3 %	≤ 3 %	
% crystallinity	87 %	74 %	(ISO 13779-3)
Trace elements:			ASTM F1185-03
As	< 3 ppm	< 1.5 ppm	
Cd	< 3 ppm	< 1.5 ppm	
Hg	< 3 ppm	< 1.5 ppm	
Pb	< 10 ppm	< 10 ppm	

Microstructure

In Fig. 3a, the SEM image of the HA coated PEEK implant revealed a rough coating which cover completely the underlying substrate. High magnification micrograph of the HA coating showed the classical inhomogeneous surface morphology and microcracks (Fig. 3b). The morphology of the HA indicates that the HA was partly melted during impact onto the surface.

It is confirmed by the relatively low crystallinity rate of 74 % (compared with 87 % for Ti-6Al-4V). Crystallographic composition of the HA coating was investigated by X-Ray diffraction. The spectrum showed hydroxyapatite (JCPDS 9.432) as a main component. No characteristic peaks of α-tricalcium, β-tricalcium, tetracalcium phosphate (TTCP) or calcium oxide (respectively JCPDS 9.348, 9.169, 25.1137 and JCPDS 4.777) were detectable (Fig. 4). Furthermore, Ca/P ratio (Ca/P = 1.694) is close to the Ca/P ratio of pure hydroxyapatite (Ca/P = 1.667). These results are in good accordance with the results obtained with Ti-6Al-4V: the spectrum showed a small TTCP peak (040) at d = 2.995 Å.

a)



b)

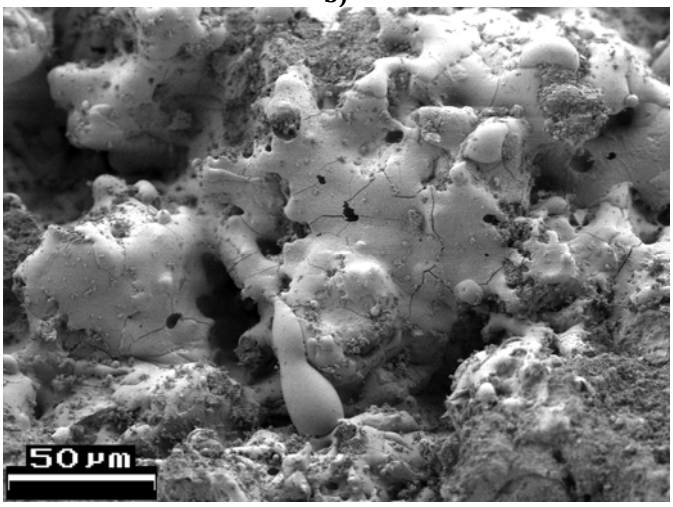


Figure 3a and 3b: SEM view of HA coating on PEEK prototype (with a tilt of 30°).

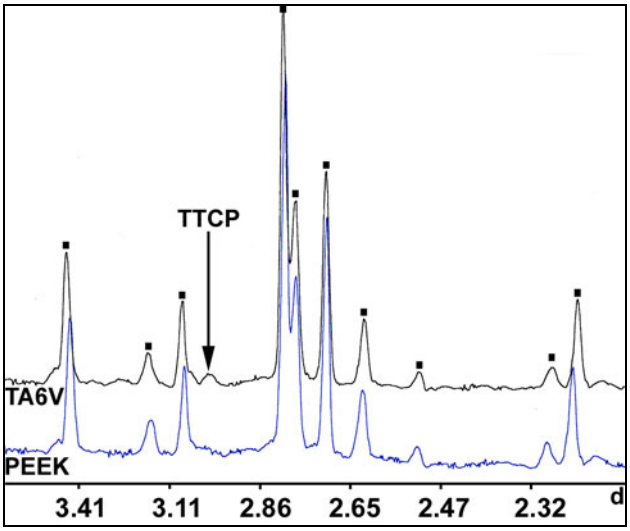


Figure 4: XRD spectrum of hydroxyapatite coating on PEEK and on Ti-6Al-4V (TA6V).

In fact, the morphology (porosity and roughness) of the HA coating on PEEK, on CF/PEEK and on Ti-6Al-4V samples were appreciably equivalent (Figs. 5a, 5b and 5c). The results concluded that changing the material substrate did not affect the composition of the HA coating.

Table 2: Adhesion and microstructural properties of HA sprayed on Ti-6Al-4V, on PEEK and on CF/PEEK.

	HA on Ti-6Al-4V	HA on PEEK	HA on CF/PEEK	Standard
Adherence	18 MPa	7.5 MPa	-	ISO 13779-4
Substrate roughness: Ra Rt	 5.2 µm 46 µm	 5.2 µm 36 µm	 6.5 µm 29 µm	NF S94-071
Coating roughness: Ra Rt	 9 µm 60 µm	 10 µm 65 µm	 11 µm 75 µm	NF S94-071
Thickness	164 µm	158 µm	128 µm	NF S94-069
Porosity (± 1 %)	5 %	5 %	5 %	Quantitative Image Analysis

Interface

The grit blasting step could severely damage the polymer and the carbon fibers: the scraps at the interface could reduce drastically the adhesion [4]. Coating cross-section analyses revealed a good interlocking between the hydroxyapatite, the PEEK and the carbon fiber (Figs. 6 and 7). Very few alumina particles were noticed at the interface (Fig. 7b). The presence of alumina particles (5 % linear of the interface for PEEK and < 1 % for CF/PEEK) was very below the commonly requirements (15 % linear). No formation of voids or cracks indicated that the process did not damage the polymeric substrate. It is therefore assumed that this good quality of the interface results in suitable adhesion strength.

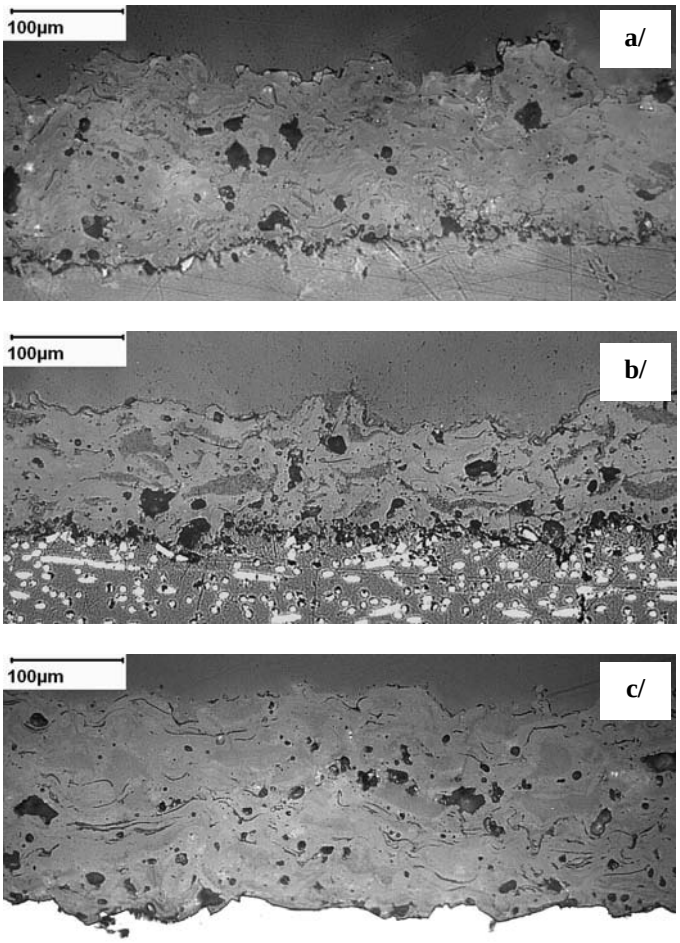


Figure 5a, 5b and 5c: Optical view of cross-sections of a/ HA coating on PEEK; b/ HA coating on CF/PEEK; c/ HA coating on Ti-6Al-4V.

Adhesion

The measurement of the tensile adhesion strength showed that the adhesion between the HA coating and the unfilled PEEK substrate was 7.5 MPa. This value is low in comparison with 18 MPa for Ti-6Al-4V. But from the implantable medical device industry point of view, a value of 7 MPa was acceptable for HA coating on metallic implants 10 years ago.

Moreover, the polymerization at 180°C during 2 hours must damage the coating and the interface because of the thermal stresses and the difference of coefficient of expansion.

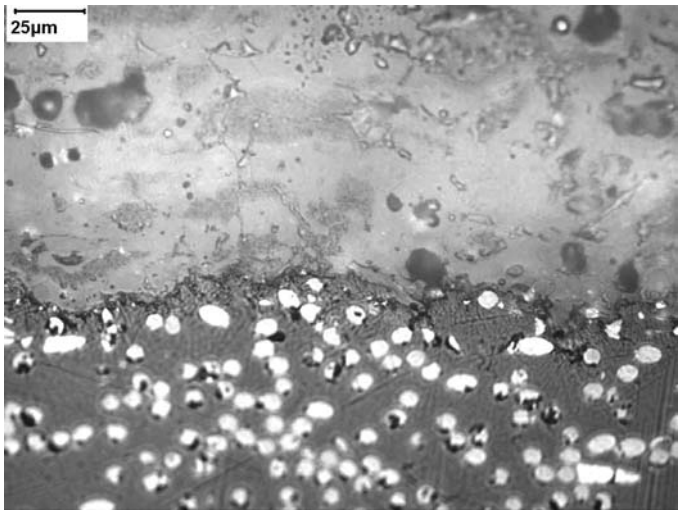


Figure 6: Optical view of the interface between the HA coating and the CF/PEEK substrate.

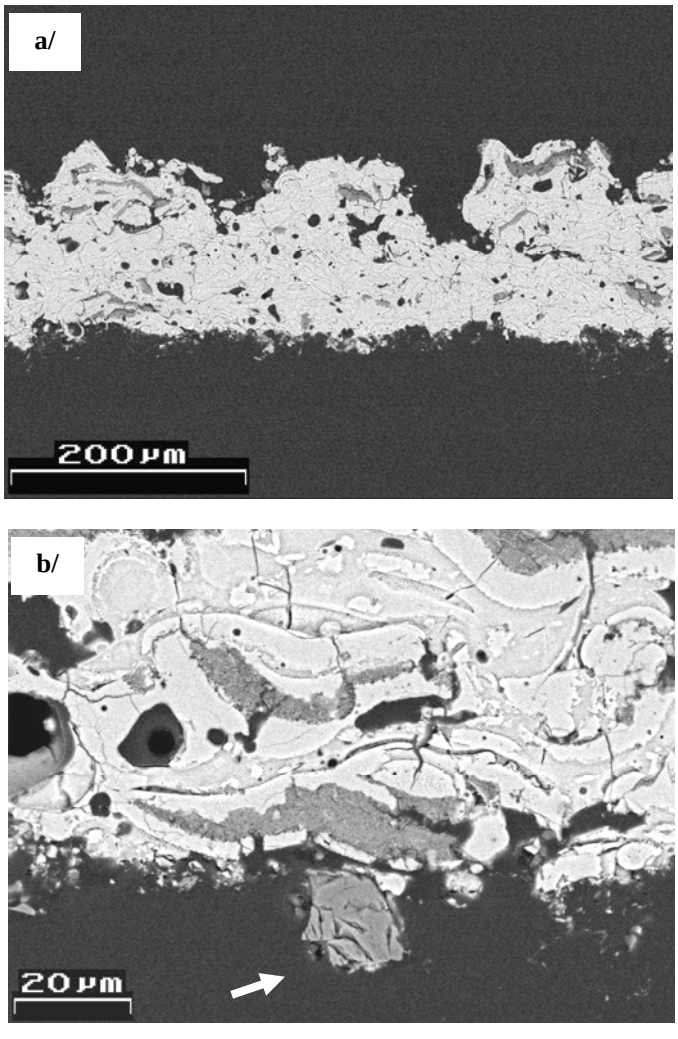


Figure 7a and 7b: BSE views of cross section of HA coating on PEEK (b: alumina particle present at the interface).

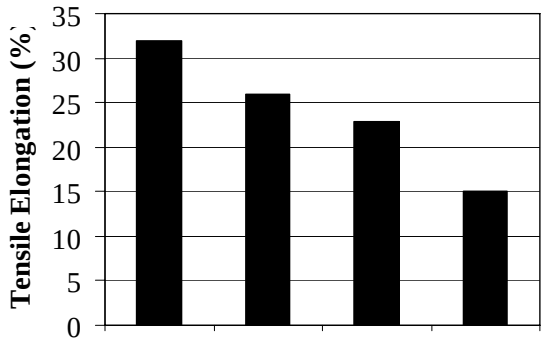
Mechanical Properties

Tensile and flex bars were coated in order to understand the effects of plasma spraying process on PEEK. Tensile strength, tensile elongation, notched Izod impact strength, flexural modulus and flexural strength were measured with and without HA coating (Table 3).

Table 3: Mechanical properties of pure PEEK and HA coated PEEK.

	PEEK	HA coated PEEK	Test Method
Tensile Strength	94 MPa	92 MPa	ISO 527
Tensile Elongation	32%	15%	ISO 527
Notched Izod Impact Strength	7.8 KJ/m²	8.2 KJ/m²	ISO 180
Flexural Modulus	3.7 GPa	4.4 GPa	ISO 178
Flexural Strength	151 MPa	169 MPa	ISO 178

The application of HA coating resulted in slightly elevated values for impact strength, flexural modulus and flexural strength. The biggest change was observed for tensile elongation which decreased from 32 to 15 %. Plasma generates a lot of irradiation such as UV. The decrease of PEEK Tensile elongation could be explained by the UV exposure [9].



Grit-blasted	-	**X**	**X**	**X**
Plasma Exposed	-	-	**X**	**X**
HA coated	-	-	-	**X**

Figure 8: Tensile Elongation for PEEK, grit-blasted PEEK, grit-blasted and plasma exposed PEEK, HA coated PEEK.

To investigate the influence of grit-blasting, plasma exposure and coating building-up, additional specimens were only grit-blasted. After, 50 % of these specimens were exposed in front of the plasma torch without powder injection. The results are presented in Fig. 8. Each step of the process affected tensile

elongation. The most important was the impacts of partly melted droplets on PEEK surface, then grit-blasting and finally plasma exposure. It is the end-users responsibility to determine if the resultant tensile elongation is acceptable for its device application.

Summary and Conclusion

Due to its bioactive behavior *in vivo*, hydroxyapatite (HA) coatings are used to improve the bone growth and repair around metallic implant. The objective of this work is to study the feasibility of plasma sprayed hydroxyapatite coating on PEEK implant. Different PEEK (unfilled and composite) specimens have been successfully coated with a 150 µm thick coating. Chemical and crystallographic compositions, adhesions and microstructures of HA coatings on PEEK and on Ti-6Al-4V were compared. The results show that the structure of HA coatings are appreciably equivalent. Mechanical tests show that the plasma spraying process does not severely degrade the initial PEEK properties, except tensile elongation. In the future, the same types of mechanical characterization will be performed with CF/PEEK.

Further work will enable to obtain better measure of the adhesion between polymers and coatings. Assessment of glues with high viscosity and which polymerizes at ambient temperature are necessary to provide a valid assessment. An improvement of the adhesion level could be obtained thanks to an optimization of the grit blasting step or the use of vacuum-plasma sprayed titanium bond coat [5]. Furthermore in vitro experiments are still in progress to study the cellular response.

The results of this study demonstrated that implantable grade PEEK can be successfully coated with hydroxyapatite. This ability will allow more versatility for the future design and development of medical devices.

Acknowledgements

Special thanks to Dr J. Devine and Mrs. I. Sinz from the Invibio Company who made available PEEK-OPTIMA® samples and carried out mechanical experiments on specimens coated by TeroLab. Dr V. Guipont and Mrs. N. De Dave Fabregue from the “Ecole des Mines de Paris, U.M.R. CNRS 7633” Laboratory are gratefully acknowledged for their SEM observations of specimens coated by TeroLab.

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