High Adhesion Plasma-Sprayed HA Coating on PEEK and Other Polymers

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Statement of Purpose: Atmospheric plasma spraying (APS) is one of the most common ways to apply an osteoconductive coating on bone implants. This process has been used extensively on metallic surfaces, but has not been used on temperature-sensitive materials such as polymers, including polyetheretherketone (PEEK), due to the extreme temperatures (thousands of degrees) the projected material reaches during APS. These temperatures exceed by far the degradation temperature of any polymeric materials, potentially causing extensive damage to the polymer surface. This damage prevents to obtain well adhered coatings that complies with standards, set for medical device coatings (ISO 13779 describing HA coatings on surgical implants), which are mainly Ca/P atomic ratio of 1.67, minimum crystalline HA content of 45%, maximum level for other crystalline phases of 5% and pull test adhesion higher than 15 MPa. This paper presents a novel preparation technique (patent pending) that permits to conventionally plasma spray hydroxylapatite (HA) coatings on PEEK and other polymers as well as key characteristics of these coatings.

Methods: The polymers used were injection grade unreinforced PEEK (Optima, Invibio, UK) and carbon-fiber (CF) reinforced PEEK (grade 150CA30, Victrex, USA), as well as a long CF reinforced polyamide 12 (CF/PA12, Schappe Techniques, France). The polymers were molded into plates according to the manufacturers' recommenddations. Prior to APS, a 100µm-thick film, composed of 30%wt. HA particles (Captal 30, Plasma Biotal, UK) and PA12 or PEEK, was overmolded at the surface of the respective polymer substrate. Coatings of HA (*ibid.*) were produced by APS on substrates using a SG-100 plasma gun (Plasmadyne, Geotel Co., USA) with a current of 500 A and Ar flow rate of 60 L/min. Coating thickness was nominally 85 µm but higher thicknesses were also produced. X-ray diffraction (XRD, D8 Discovery Diffractometer, Bruker AXS, USA; Copper $K_{\alpha 1}$, θ-2θ configuration, 40 mV and 40 mA) analysis for composition and crystallinity was performed on the coatings. Crystalline index (I_c) was obtained from the ratio between the sum of crystalline peak area and the total spectrum area. Polished cross-sections were also examined using a scanning electron microscope (SEM-FEG, Hitachi S-4700, Hitachi Canada) and energy dispersive spectroscopy (EDS) at 20 KV. Pull and lap shear tests were performed according to ASTM F1147 and F1044, respectively. Lap shear tests were added because they are more representative of *in-service* mechanical conditions of the coated implant.

Results: XRD analysis was first carried out on the APS HA coatings of all polymer substrates. It was found that the coating had a crystalline index of 0.53 ± 0.01 and that HA, as defined by the Joint Committee on Powder Diffraction Standards #9-432, was the only crystalline phase present. SEM/EDS revealed that HA coatings (Fig. 1) had an inherent porosity, typical of APS (≈8-9%), showing a coherent coating-substrate interface and a Ca/P atomic ratio of 1.66 ± 0.02. Pull tests were performed on the different polymer substrates. Mechanical adhesion obtained was 20.5 ± 0.07 MPa for PA12/CF and 20.9 ± 2.1 for PEEK/CF. All specimens broke adhesively, *i.e.,* at the coating/substrate interface. Lap shear tests were performed for different coating thicknesses. Shear strength (Fig. 2) varied from 17.7 ± 2.7 MPa for 350-380µm-thick coatings to 25.2 ± 1.2 MPa for 80-85µm-thick coatings, showing a decrease in strength for thicker coatings due to their cohesive mode of failure.

In general, the coatings surpass the standards set for medical device HA coatings, *e.g.,* crystalline index of 0.53 associated to HA peaks, absence of other crystalline phases, Ca/P ratio of 1.66, and pull test adhesion above 20 MPa. Shear strength of HA coating also considerably exceeds typical values of 5-8 MPa reported for HA coatings on metallic implants [1].

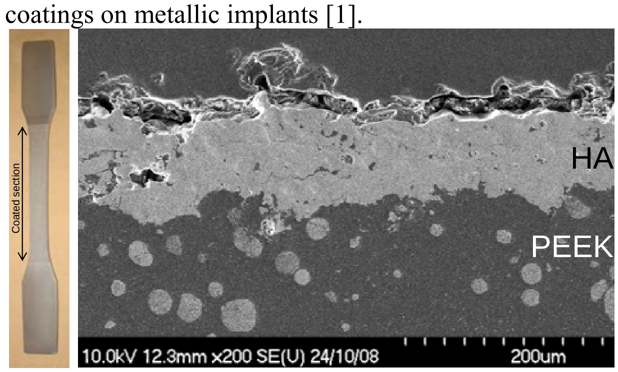

Fig. 1 (*left*) PEEK dogbone with HA coating (arrow) and (*right*) cross-section of PEEK with HA coating.

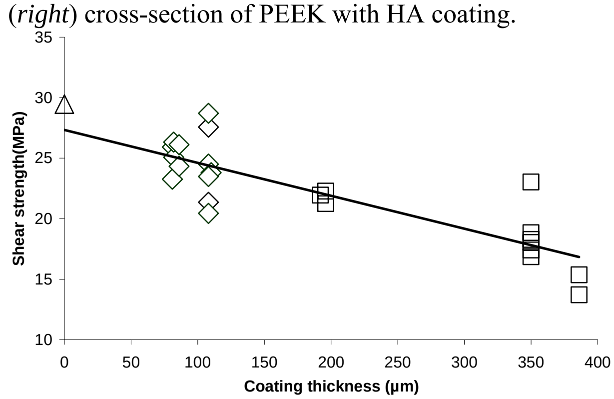

Fig. 2 Shear strength vs. HA coating thickness. Symbol ◇ indicate adhesive failure and □ a cohesive failure. Symbol △ refers to epoxy-PA12/CF without HA coating.

Conclusions: A novel preparation method (patent pending) was used to conventionally plasma spray HA coatings on temperature sensitive materials such as PEEK or PA12. The physico-chemical and mechanical characteristics obtained underline the excellent quality of the HA coatings on polymers using the proposed method.

Reference: 1. Kusakabe H. Biomater. 2004;25:2957-69.

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