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# Plasma-sprayed hydroxylapatite coating on carbon fibre reinforced thermoplastic composite materials

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Plasma-spraying of metallic implant surfaces is an established method for the application of hydroxylapatite (HA) coatings. Carbon fibre reinforced thermoplastics show different thermal and mechanical properties, compared with titanium substrates. In this paper first results of the influence of the established coating method on carbon fibre reinforced thermoplastics are presented. First investigations of the tensile adhesion strength, tested with a newly developed testing device, showed that the adhesion between the HA coating and the carbon fibre reinforced polyetheretherketone (PEEK) composite is very low. Macromechanical bending tests showed a change to initial tensile instead of compression failure of the coated composite substrate. Micromechanical bending tests in a scanning electron microscope (SEM) hot tensile stage (Raith GmbH) revealed crack propagation within the ceramic coating and in the coating–substrate interface before the total failure of the composite substrate occurred.

## 1. Introduction

Long-term performance and stability of load bearing implants require a high degree of biocompatibility. One of the most important features of the application of any load bearing devices within the human body is that the device disturbs the pattern of load transfer as little as possible, because the bone structure is strongly related to the stress fields and stress distribution [1]. Structure compatibility can be expected by using an anisotropic implant material with similar structure behaviour, since the structure of bone is highly anisotropic [2]. Surface compatibility between the recipient tissue and the implant surface can be enhanced by coating the implant material with a bioactive material [3, 4]. Due to its bioactive behaviour *in vivo*, HA has a growing significance for the application as a coating material for implant devices [5–9]. Plasma-spraying of HA coatings on titanium implants, such as hip joint and knee endoprostheses, is a currently established method to improve the surface compatibility and has also been applied successfully on poly(L-lactide) [10, 11]. In this work preliminary investigations of the influence of the plasma-spraying process on the mechanical properties of carbon fibre reinforced thermoplastics are presented.

## 2. Materials and methods

### 2.1. Materials

Unidirectional $(0_8, 90_8)$- and angle ply $(0, +45, -45, 0)_{2S}$-carbon fibre reinforced PEEK (APC-2, ICI) samples were fabricated by hot pressing. Using image processing analysis [12] the fibre volume fraction of the APC-2 composite was measured to be 59 vol %. The 1 mm thick specimens were first sandblasted and then coated with a layer of 200 μm of HA by plasma spraying. PEEK has a very low thermal conductivity of $\lambda = 0.25\ \mathrm{W(mK^{-1})}$ [13], compared with titanium alloys: $\lambda_{Ti6Al4V} = 6\ \mathrm{W\,mK^{-1}}$ [14]. Glass transition and melting temperature of PEEK are $T_g = 143\,^\circ\mathrm{C}$ and $T_m = 334\,^\circ\mathrm{C}$, while a melting temperature of 1650 °C for HA is reported in [15].

### 2.2. Mechanical testing

The mechanical testing included macroscopic and microscopic investigations, using the three-point bending method, according to DIN 29971 [16]. The macroscopic tests were performed with a universal testing machine (Zwick 1474) to evaluate the failure characteristics of the coated composite and the bending of the HA-coating. Specimens were tested with a span-to-depth ratio of 40:1 and a crosshead speed of 6 mm min$^{-1}$. Micromechanical analyses were made using a three-point bending device in the SEM hot tensile stage, with a span-to-depth ratio of 16:1 and a crosshead speed of 1.2 mm min$^{-1}$. This method enables the observation of the crack propagation while performing SEM analysis. The HA-coatings were tested on the tensile side of the composite in all mechanical bending investigations.

#### *2.2.1. Scanning electron microscopy (SEM)*

SEM investigations were made to analyse the influence of the plasma-spraying process, including pretreatment by sandblasting, on the composite surface. The failure behaviour of the coated composites was analysed on-line, using the SEM hot tensile stage, as mentioned above.

### 2.2.2 Adhesion measurement

To measure the tensile adhesion strength of the HA-coating on the composite substrate, a new testing device, called an orthogonal-pull-off device (OPD), has been developed, in reference to DIN 50160 [17]. A schematic diagram of this device is shown in Fig. 1.

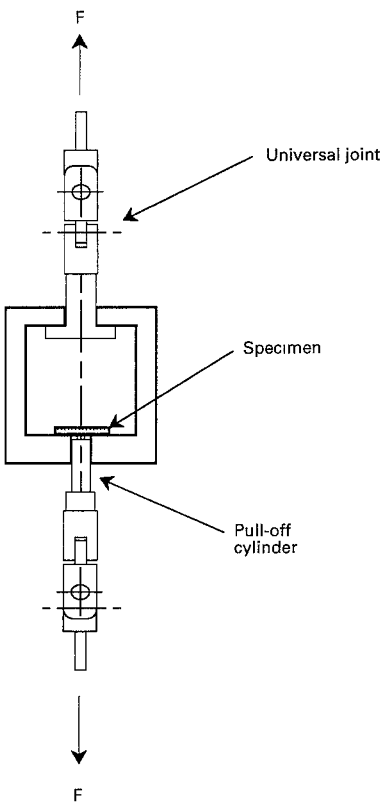


*Figure 1* Orthogonal pull-off device (OPD) for the measurement of the tensile adhesion strength

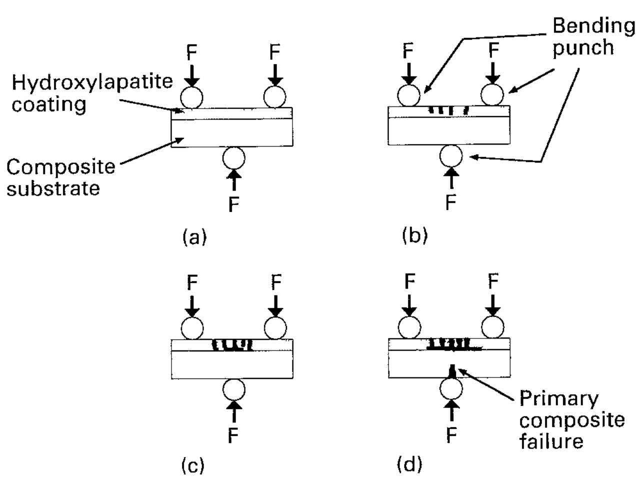


*Figure 2* Schematic diagram of different loading states during the microscopic three-point bending testing in the SEM hot tensile stage with the HA-coating being loaded on the tensile side. The load was increased continuously from (a) to (d) until composite failure occurred: (a) starting state; (b) crack initiation at the coating surface; (c) crack propagation and starting of coating delamination; (d) primary composite failure.

This method enables the testing of coated composite materials with different shapes. The pull-off cylinders were glued on the coating with a cyanoacrylate gel (Balcozin-Gel) of high viscosity (Fig. 2). First results were achieved by testing five samples.

## 3. Results and discussion

The result of the macroscopic three-point bending test showed that primary failure of the coated $0_8$-specimens occurred on the tensile side of the coated composite substrate, whereas it was expected to occur at the compression side. SEM investigations showed that several carbon fibres at the outer layers were severely damaged in the plasma-spraying process, including pretreatment by sandblasting (Fig. 3). This could be an indication of a weakening of the substrate surface due to the plasma-spraying process including sandblasting. It was observed that the HA-coating loaded on the tensile side could be highly bent, which was first attributed to the microcracks present in the coating (Fig. 5). However, three-point bending tests in the SEM hot tensile stage showed that a crack propagation appeared within the coating followed by coating delamination. The cracks were observed to initiate from the coating surface, propagating towards the coating-substrate interface (Fig. 6). The total delamination of the HA-coating occurred after the failure of the composite material (Fig. 7). It was observed that the HA-coating of the unidirectional specimens partly peeled off at the same time as the composite failure, while this fact was not observed with the angle-ply

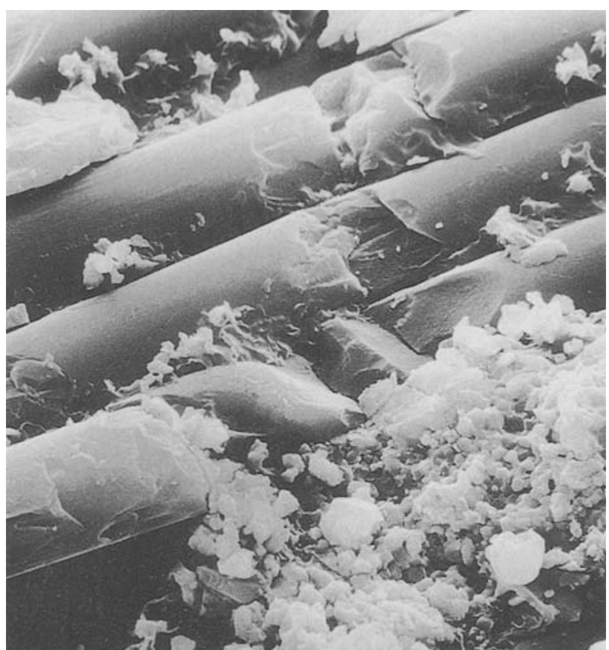


*Figure 3* Carbon fibres after plasma-spraying process, including sandblasting. Several carbon fibres at the outer layers were severely damaged.


*Figure 4* Composite surface after delamination of the HA-coating. The surface of certain carbon fibres have partially matrix-free domains.


*Figure 5* High magnification micrograph of the HA-coating showing the inhomogenous surface morphology and microcracks. The morphology of the HA-coating indicates that the HA was at least partly melted during impact onto the substrate surface.

specimens. It was seen in SEM that the polymer surface of the composite was mostly removed during the plasma-spraying process including sandblasting, meanwhile the matrix between the fibres was melted

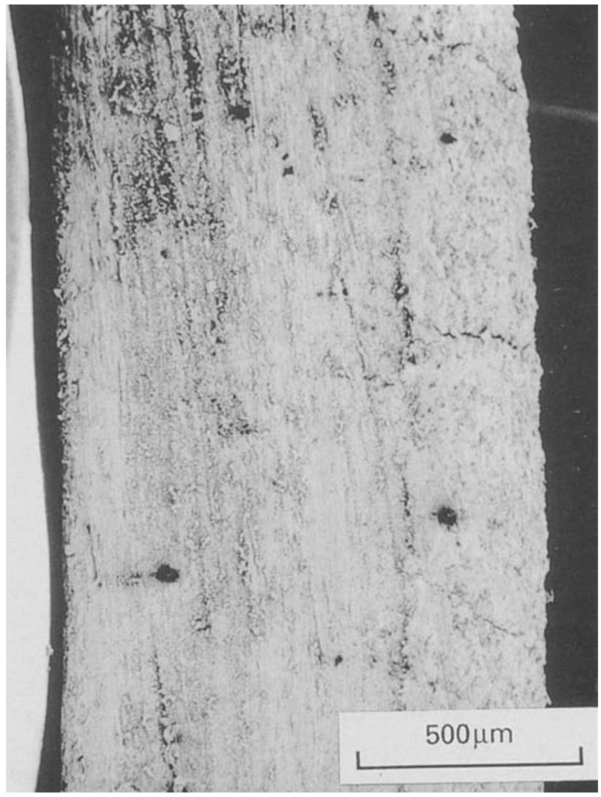


*Figure 6* Crack propagation within the HA-coating during the three-point bending measurement in the SEM tensile hot stage. The cracks start at the coating surface and propagate to the coating–substrate interface, initiating delamination of the HA-coating (schematically shown in Fig. 2b and 2c).

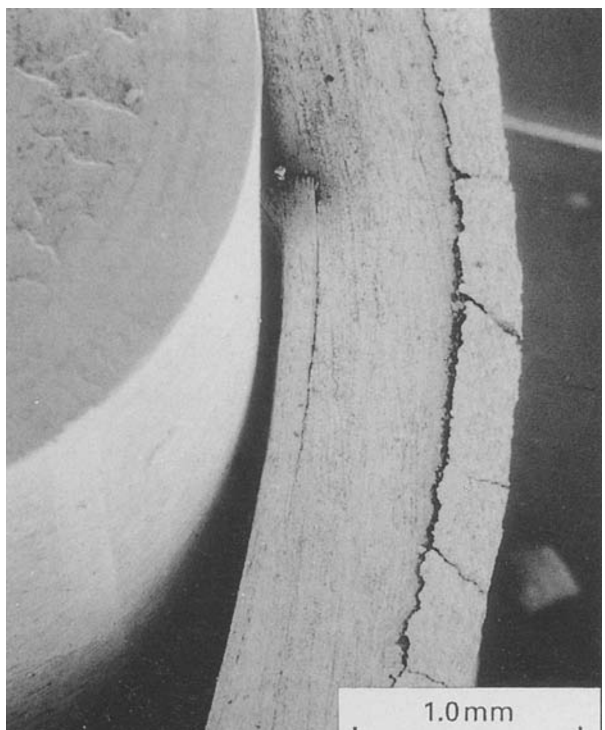


*Figure 7* Microscopic primary compression failure of the angle-ply composite substrate, subsequently followed by the definitive delamination of the HA-coating (schematically shown in Fig. 2d).

(Fig. 4). The measurement of the tensile adhesion strength with the orthogonal-pull-off device showed that the adhesion between plasma-sprayed HA-coating and carbon fibre reinforced thermoplastic composite is low. It was measured to be 2.8 MPa.

## 4. Conclusions

Investigation of the tensile adhesion strength showed that adhesion of the plasma-sprayed HA-coating on the substrate of the carbon reinforced thermoplastic composite is very low. It is suggested that the impact of the first HA-particles, being partly melted at a temperature above 1650 °C, cause evaporation of the underlying PEEK-matrix, producing a vapour film, which could partially prevent close contact of the HA coating with the substrate, resulting in low coating–substrate adhesion. The optimization of the parameters of the plasma-spraying process could lead to higher adhesion strengths. The macroscopic investigations indicate high tolerance against increasing elongation of the HA-coating loaded on the tensile side, while micromechanical testing in the SEM hot tensile stage revealed a "pseudo-subcritical" crack propagation. This means that the present microcracks could have contributed to stepwise crack propagation within the HA-coating and in the coating–substrate interface before total failure of the composite occurred. While macroscopic bending tests of the coated composite specimens showed failure on the tensile side, primary failure in the microscopic bending tests occurred on the compression side. This fact gives rise to further investigations.

## 5. Outlook

Further research work will include optimization of the currently used plasma-spraying process as commercially applied to titanium surfaces, including investigation of the influence of sandblasting on the substrate composite, chemical investigations of the substrate and, in particular, the PEEK-matrix before and after the plasma-spraying process, and further mechanical investigations. It is expected that by optimization, desirable surface coating of carbon fibre reinforced thermoplastics can be achieved and that increased surface compatibility for load transmitting orthopaedic implants will result.

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