Mechanical Properties and Bioactivity of PEEK-OPTIMA®/Hydroxyapatite Compounds

[1]Brady M., [2]Poulsson A.H.C., [1]Wilson J., [2]Eglin D., [2]Richards R.G., [1]Jarman-Smith M.
[1]Invibio Biomaterial Solutions, Thornton-Cleveleys, UK; [2]AO Research Institute, Davos, CH.

Statement of Purpose: PEEK (polyetheretherketone) is widely used as a medical implant material due to its biocompatibility, advantageous mechanical properties and high chemical resistance[1]. In more recent years, interest has grown in compounding PEEK with bioactive materials such as hydroxyapatite (HA) to further improve bone fixation. However, frequent compromise is observed with respect to the mechanical properties and potential for scalable production. Here we describe an industrially relevant process for the production of PEEK, containing HA as a bioactive component. This study aims to identify the optimal filler content, which maintains mechanical properties close to that of the unfilled PEEK, as well as imparting increased bioactivity.

Methods: PEEK-OPTIMA® (Invibio Biomaterial Solutions, UK) was dried to remove the 0.5% of water which it absorbs, and twin-screw compounded at 360-400°C with hydroxyapatite (mean particle size 5µm, Plasma Biotal Ltd., UK) whilst the polymer was in a fluid state to obtain a HA fill in the range 10-50% by weight. A normal screw profile fabricated from stainless steel was used with a minimum L/D ratio of 45:1. At the extrusion end a twin hole die with a 4mm orifice and pelletizer was used. The main screw rotation speed was set at 150-250 rpm. The resulting compounded granules were injection moulded and mechanical properties, including impact strength (ISO 180), flex strength (ISO 178), flex modulus (ISO 178), tensile strength (ISO 527), and strain at break (ISO 527), were determined and compared with those of unfilled PEEK controls. Bioactivity of the PEEK/HA was determined by the ability to form apatite on the surface of the material in a simulated body fluid (SBF-JL2) described in Bohner *et al.*[2], and compared with PEEK controls. Samples were immersed in SBF for 1, 3 and 7 days on a rotating platform at 37°C with 5% CO_2 and 100% humidity. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were used to analyze the bioactive elements present on the surface of the specimens following immersion in SBF.

Results: PEEK was successfully compounded with HA up to 50% fill by weight, without significant issue and with no reaction observed between the two components. The mean mechanical values for impact strength, flex strength, flex modulus, tensile strength, and strain at break were plotted against the filler content and compared with those of the unfilled PEEK to determine optimum fill as shown in Table 1. PEEK-OPTIMA containing 20% HA by weight was chosen for further bioactivity studies due to the limited effects on material mechanical properties.

SEM analysis of the surface of PEEK controls and PEEK/20%HA composite revealed the formation of spherical crystals on the surface after immersion in SBF.

Table 1. *Mechanical properties of PEEK-OPTIMA with HA filler content in the range 10-50%. Properties of the compound with optimal filler content are shown in red.*

Property	PEEK - OPTIMA	10% HA	20% HA	30% HA	40% HA	50% HA
Impact (KJ/m2)	**7.33**	7.4	6.1	5.2	4.6	4.6
Flex Strength (MPa)	**162.45**	156.1	156.0	154.2	139.2	118.8
Flex Modulus (GPa)	**3.96**	4.33	4.72	5.61	6.67	8.02
Tensile Strength (MPa)	**99.25**	88.7	88.7	81.8	73.5	75.5
Strain at Break %	**35.8**	24.09	8.8	3.98	2.24	1.27

These were more numerous and apparent on the PEEK/20%HA samples and these were observed as early as 1 day post-immersion in SBF, suggesting increased apatite formation.

Detailed Ca2p and P2p XPS spectra revealed that although Ca and P were identified on the surface of both materials, only elemental ratios present on the PEEK/20%HA samples were conducive to bone formation with a Ca/P ratio of 1.66, close to the theoretical value for hydroxyapatite. Meanwhile, the ratios of the depositions on the control PEEK were more variable (>1.67), and indicative of non-hydroxyapatite calcium phosphate formations..

Following immersion in SBF for 1 day, ATR-FTIR surface analysis was performed on PEEK/20%HA and control samples to semi-quantify the degree of apatite deposition and detect functional groups. A significant peak was observed at 1015 cm^{-1}, most likely arising from the structural P-O bond of phosphate groups. The ratio of absorption at 1015cm^{-1} to 1645cm^{-1} (characteristic of PEEK) was measured and showed an increased ratio on PEEK/20%HA samples compared with control PEEK, confirming the XPS findings indicating greater apatite formation on the PEEK/20%HA samples.

Conclusions: The study describes an industrially relevant route for the production of a PEEK/HA (20% by weight) compound through twin-screw compounding, without significant loss of the advantageous mechanical properties of PEEK. Additionally we have demonstrated increased Ca/P deposition of this compound following immersion in SBF, indicative of the potential for increased bony integration *in vivo*. It is hoped that further *in vitro* studies examining osteoblast-mediated mineralization will further elaborate these findings.

References:

[1]Kurtz S.M. Biomaterials. 2007;28(32):4845-4869
[2]Bohner M. Biomaterials. 2009;30(12):2175-2179