Hydroxyapatite Coating on PEEK: Material Processing, Analysis and Biocompatibility Study

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Statement of Purpose: Poly-ether-ether-ketone (PEEK) is a highly heat resistant thermoplastic with excellent strength and elastic modulus close to human bone that can offer reduced risk of stress shielding and bone loss if used as implants. PEEK exhibits high chemical and thermal stability; implants can be sterilized by gamma-irradiation, ethylene oxide or steam autoclaving without experiencing any significant hydrolytic decomposition or losing their mechanical strength. In addition, PEEK is radiolucent, when examined by plain film radiography, computed tomography or magnetic resonance imaging, a property that is particularly useful when the primary intent of these imaging modalities is to examine the healing response of peri-implant tissues (bone and soft tissue). PEEK implants have become widely accepted as alternatives to metal implants in spine surgery. PEEK has been shown to perform well with minimal evidence of adverse tissue responses. However, the hydrophobic surface of PEEK implants induces fibrous encapsulation that impedes bone apposition, which is unfavorable for stable anchorage of implants. One potential solution is to coat PEEK implants with a thin layer of bioactive calcium phosphate coating such as HA or hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). HA is traditionally applied by plasma-spraying, which involves high temperatures that can damage PEEK. Furthermore, these coatings lack strong adhesion to their substrate and mechanical robustness. This research involves a method for coating PEEK with a two-layer design consisting of Yttria-stabilized Zirconia (YSZ), as a heat-protection layer over PEEK, and an HA top layer, to achieve better osseointegration and improved bioactivity *in vitro*.

Methods: The coatings were deposited on flat, polished PEEK (Invibio, Lancashire, UK) substrates via ion beam assisted deposition (IBAD). In this case, the secondary ion bombardment of the substrate during deposition further improved the interfacial strength via atomic mixing. YSZ and HA sputter targets were used in succession to achieve the two-layer structure. The deposition temperatures were monitored and regulated below the glass-transition temperature of PEEK to avoid any damage to the substrate. Post-deposition microwave heat treatment was performed in combination with a hydrothermal treatment in a variable-frequency microwave oven and a commercial autoclave to crystallize the HA layer. The bond strength of the coating was analyzed using the pull-off method with epoxy-coated studs and a pull-down breaking point platform. The microstructure and chemical composition of the coating was analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The cell culture study was performed on four test groups: one uncoated PEEK, one as-deposited coating (AD), and two coating with heat treatments (HT1, HT2). An *in vitro* study was conducted using MC3T3 osteoblast cells to investigate cell growth, proliferation, differentiation and mineralization followed by statistical analysis.

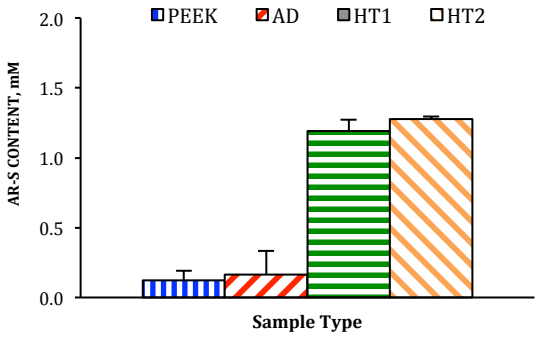

Figure 1: Biomineralization Data

Results: SEM images show that the two-layer coating deposited has a total of 2μm thickness, consisting of 1μm YSZ and 1μm HA. The average bond strength of the coating was measured to be about 40MPa on a smooth surface, greatly exceeding the 15MPa benchmark for HA coatings as prescribed by the ISO13779-2 standard. This has been increased to over 70MPA by altering the surface finish of PEEK. XRD analysis of the as-deposited coatings indicated a crystalline YSZ and an amorphous HA layer prior to any heat treatment. Hydrothermal and microwave processing techniques were utilized to crystallize the HA layer and further improve bioactivity without damaging the PEEK substrate. The XRD analysis of samples that underwent heat treatment confirmed crystallization of the HA layer. The *in vitro* study showed significantly higher mineralization on heat-treated samples versus PEEK/AD groups as observed in Figure 1.

Conclusions: In this study, a two-layer YSZ-HA bioactive coating was deposited on PEEK using an IBAD technique with enhanced adhesion strength compared to coatings deposited using other methods. During heat treatment, the YSZ layer promoted crystallization of the HA layer by providing nucleation sites as well as protecting the underlying PEEK from excessive heat. Hydrothermal treatment induces crystallization with temperature and pressure. PEEK is a microwave transparent material, not directly heated by the microwave irradiation, YSZ absorbs more irradiation and HA exhibits the highest of all three. As a result, the layered structure provided a gradient of microwave absorption and protected the PEEK from thermal degradation during heat treatment and debonding of the coating due to the mismatch in coefficient of thermal expansion between PEEK and HA. As evident by XRD and SEM analysis, a combination of these heat treatments was capable of crystallizing HA at reduced temperatures. The *in vitro* study reveals enhanced bioactivity by coating PEEK with YSZ-HA and heat treatment of the coatings produces the best bioresponse. The mechanical performance, material analysis and cell culture study show that this method of coating is promising for orthopedic and spinal implants where a robust, bioactive surface is necessary.