

Bioactive Surface-porous PEKK

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Introduction: Polyaryletherketones (PAEK) have been increasingly used as spinal and orthopedic implants because of their physicochemical, radiolucent and mechanical properties. However, PAEKs are bioinert and have limited osseointegration ability. Methods to improve the bioactivity of PAEK include coating of PAEK implants with bioactive materials, plasma modification, chemical grafting and etching, and introduction of porous structures. As a member of PAEKs family, polyaryletherketoneketone (PEKK) has better thermal stability, mechanical property and more double bond (C=O) available for modification than PEEK. In the present study, we developed a novel method to prepare bioactive surface-porous PEKK materials and evaluated their material properties and *in vitro* biological performance.

Materials & Methods: Figure 1. shows the process diagram to prepare bioactive surface-porous PEKK. PEKK powder, spherical hydroxyapatite (HA) particles (~300 - 800 μm) and ethanol were mixed to develop slurries, which were poured into a self-made mold and hot-pressed at 400°C to form PEKK/HA composites. Then, the HA particles were dissolved by immersing the composites in a 37wt% HCl solution for 3 hr to obtain porous PEKK (PEKK-P). The PEKK-P samples were modified by etching in 80% sulfuric acid for 3 hr (PEKK-SP) and then immersed in a simulated body fluid (SBF) at 37°C for 5 d to prepare the bioactive surface-porous PEKK (PEKK-BSP). With the same fixture and thermal process, dense PEKK disks, PEKK-S and PEKK-BS were also prepared after molding PEKK powder, etching in sulfuric acid and immersing in a SBF sequentially. Physical and chemical properties of samples were characterized by microCT, scanning electron microscope (SEM), mercury intrusion porosimetry, water contact angle, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and uniaxial compression test machine. The confocal laser scanning microscope, MTT assay and real-time quantitative polymerase chain reaction (qRT-PCR) were used to analyze the biological response of the samples using rabbits' mesenchymal stem cells (MSCs).

Results & Discussion: The microCT and SEM observation showed that the combination of physical and chemical processes created a surface-porous PEKK material (PEKK-SP) that had both structurally interconnected and open macropores (200 - 600 μm) due to templating of HA microspheres, and micropores (< 10 μm) due to effects of the sulfonation. The contact angle of a hydrophobic PEKK disk sample ($92.7 \pm 2.3^\circ$) was significantly reduced to hydrophilic nature after sulfonation ($53.6 \pm 5.3^\circ$) and followed by soaking in SBF

for 5d ($10.6 \pm 0.7^\circ$). The surface morphology of the specimens after soaking in SBF suggested that the formation of bone-like apatite (Figure 1). The FTIR spectra confirm that SO_3H functional groups were introduced to the porous PEKK surface after sulfonation. Mechanical tests showed that both PEKK-BSP and PEKK-P were better than PEKK-SP in terms of compressive strength and modulus. *In vitro* cell culture demonstrated that PEKK-BSP promoted better cell growth and proliferation than other groups of PEKK materials. Moreover, as compared to PEKK material alone, PEKK-BSP elevated gene expressions of osteocalcin (OCN), Type I collagen (Col-I), alkaline phosphatase (ALP), and runt-related transcription factor 2 (Runx2).

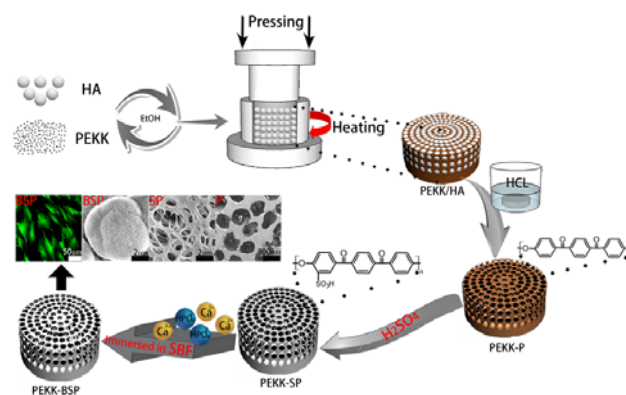


Figure 1. A schematic diagram of the process to prepare bioactive surface-porous PEKK.

Conclusion: Bioactive surface-porous PEKK materials were prepared by removing HA microsphere templates from compression molded PEKK/HA composites followed by sulfonation (PEKK-SP) and then soaking in a simulated body fluid for 5 d (PEKK-BSP). *In vitro* cell culture demonstrated that PEKK-BSP had better cell proliferation, viability as well as elevated gene expressions of OCN, Col-1, ALP, and Runx2 than those of PEKK alone (14 d). The *in vitro* bone-like apatite forming ability of the PEKK-BSP suggests its potential tissue bonding ability *in vivo*. PEKK-BSP has potential applications as spinal interbody fusion devices to enhance their potential *in vivo* osseointegration ability and fusion rate.

References:

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