

Incorporating Hydroxyapatite and Porosity in PEEK for Orthopaedic and Spine Applications

Ryan K. Roeder^{1,2}

¹Department of Aerospace and Mechanical Engineering, ²Bioengineering Graduate Program,
University of Notre Dame, Notre Dame, IN 46556.

Introduction: Polyetheretherketone (PEEK) is the most commercially prominent member of polyaryletherketones, which are semi-crystalline thermoplastic polymers exhibiting biomechanical properties suitable for load-bearing implants.¹⁻³ PEEK was originally developed and marketed in the 1980s for industrial applications as a high strength thermoplastic with outstanding resistance to chemical and thermal degradation. In the 1990s, PEEK became the leading thermoplastic for replacing metals in orthopaedic and spinal implants.

For example, interbody spinal fusion utilizes an implant inserted in the disc space to restore vertebral height, promote fusion between adjacent vertebrae and stabilize the spine. At present, PEEK has virtually supplanted titanium in this application. The high x-ray attenuation of titanium makes radiographic assessment of fusion difficult, while PEEK is radiolucent.² Moreover, the high stiffness of titanium is also believed to inhibit bone growth through the implant by shielding cells/tissue from stresses. In contrast, the elastic modulus of neat (unfilled) PEEK can match that of trabecular bone (up to 4 GPa), and carbon fiber-reinforced PEEK can be tailored to match the elastic modulus of cortical bone (16-23 GPa) and even titanium (110 GPa).³

PEEK is not without its own limitations, however. Numerous studies have demonstrated that PEEK is biocompatible.¹ However, PEEK is also bioinert, which typically leads to the formation of fibrous tissue rather than bony apposition at the implant interface. Moreover, osteoinductive growth factors are necessary to generate space-filling bone formation, as in a spinal fusion. Therefore, recent studies have investigated modifications of PEEK to promote (1) bioactivity through surface modification and/or the addition of bioactive fillers, and (2) osteointegration through the incorporation of porosity.

Hydroxyapatite: Bioactivity has been conferred to PEEK by the incorporation of calcium phosphate, typically hydroxyapatite (HA) but also BioglassTM and tricalcium phosphate, as a coating or filler. Coatings have been applied directly using plasma spray⁵ or indirectly using surface treatment to induce apatite deposition in simulated body fluid.⁶ A larger number of investigations have studied the use of calcium phosphate fillers to reinforce PEEK. This concept was predated by the pioneering work of W. Bonfield and colleagues to reinforce high density polyethylene (HDPE) with HA.⁷ However, unlike PEEK, the mechanical properties of HDPE limited application to non-load-bearing implants.

PEEK has been reinforced with up to 40 vol% HA powders by compounding and injection molding,⁸ and up to 50 vol% single crystal HA whiskers by powder consolidation and compression molding.⁹ Increased levels of HA were shown to enable elastic moduli to mimic human cortical bone,^{8,9} and improve cellular activity,¹⁰

but resulted in decreased tensile strength^{8,9} and fatigue resistance.^{8,11} Thus, important trade-offs may exist in structure-property relationships that must be defined and considered in implant design. Nonetheless, HA-reinforced PEEK offers a robust system to engineer implant biomaterials. Many aspects of the composite structure can be tailored in order to design for specific mechanical, biological, and surgical functions: the PEEK crystallinity and molecular orientation; the HA/PEEK interface; and the HA reinforcement content, morphology, preferred orientation, and size.¹²

Porosity: The requirement of interconnected porosity (70-90%, 200-400 μm) is well-known for vascularization, cell migration and bone ingrowth.¹³ Porous PEEK scaffolds were prepared using selective laser sintering, but the porosity was limited to <75% and the HA content was limited to <25 vol%.^{14,15} Compression molding and particle leaching were used to prepare PEKK scaffolds with 75-90% porosity and up to 40 vol% HA.¹⁶ The scaffold microstructure exhibited characteristics known to be favorable for osteointegration and the apparent compressive mechanical properties were able to mimic those of human trabecular bone. Thus, PEEK scaffolds may overcome the limited mechanical competency of many polymer and reinforced polymer scaffolds.

Conclusions: PEEK biomaterials offer a wide variety of opportunities for basic research and product development, which span across materials processing, nano- and microstructural characterization, surface engineering, mechanical behavior, implant design and osteointegration. The relative immaturity of PEEK as a biomaterial, combined with the rapid clinical adoption of PEEK interbody spinal fusion cages, suggests that PEEK biomaterials will find application in an increasing number of biomedical implants in the years to come.

References: ¹SM Kurtz, *et al.*, *Biomaterials*, 28:4845-4869, 2007; ²M Toth, *et al.*, *Biomaterials*, 27:324-334, 2006; ³SL Evans, *et al.*, *Biomaterials*, 19:1329-1342, 1998; ⁴SG Sagomonyants, *et al.*, *Biomaterials*, 29:1563-1572, 2008; ⁵SW Ha, *et al.*, *J. Mater. Sci. Mater. Med.*, 8:891-896, 1997; ⁶M Pino, *et al.*, *Acta Biomaterialia*, 4:1827-1836, 2008; ⁷M Wang, *et al.*, *Biomaterials* 19:2357-2366, 1998; ⁸Abu Bakar, *et al.*, *Biomaterials*, 24:2245-2250, 2003; ⁹GL Converse, *et al.*, *Biomaterials*, 28:927-935, 2007; ¹⁰L Di Silvio, *et al.*, *Biomaterials*, 23:101-107, 2002; ¹¹Kane, *et al.*, *J. Mech. Behav. Biomed. Mater.*, 1:261-268, 2008; ¹²RK Roeder, *et al.*, *JOM*, 60:38-45, 2008; ¹³V Karageorgiou and D Kaplan, *Biomaterials*, 26:5474-5491, 2005; ¹⁴KH Tan, *et al.*, *Biomaterials*, 24:3115-3123, 2003; ¹⁵KH Tan, *et al.*, *J. Eng. Med.*, 219:183-194, 2005; ¹⁶GL Converse *et al.*, *Acta Biomaterialia*, submitted.