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Research Paper

Monotonic and cyclic loading behavior of porous scaffolds made from poly(*para*-phenylene) for orthopedic applications

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ARTICLE INFO

Article history:
Received 20 June 2014
Received in revised form
2 October 2014
Accepted 6 October 2014
Available online 16 October 2014

Keywords:
Aromatic polymers
Porous
Fatigue
Orthopedics
Poly(para-phenylene)
Mechanical properties

ABSTRACT

Porous poly(*para*-phenylene) (PPP) scaffolds have tremendous potential as an orthopedic biomaterial; however, the underlying mechanisms controlling the monotonic and cyclic behavior are poorly understood. The purpose of this study was to develop a method to integrate micro-computed tomography (μCT), finite-element analysis (FEA), and experimental results to uncover the relationships between the porous structure and mechanical behavior. The μCT images were taken from porous PPP scaffolds with a porosity of 75 vol% and pore size distribution between 420 and 500 μm. Representative sections of the image were segmented and converted into finite-element meshes. It was shown through FEA that localized stresses within the microstructure were approximately 100 times higher than the applied global stress during the linear loading regime. Experimental analysis revealed the S–N fatigue curves for fully dense and porous PPP samples were parallel on log–log plots, with the endurance limit for porous samples in tension being approximately 100 times lower than their solid PPP counterparts (0.3–35 MPa) due to the extreme stress concentrations caused by the porous microarchitecture. The endurance limit for porous samples in compression was much higher than in tension (1.60 MPa). Through optical, laser-scanning, and scanning-electron microscopy it was found that porous tensile samples failed under Mode I fracture in both monotonic and cyclic loading. By comparison, porous compressive samples failed via strut buckling/pore collapse monotonically and by shearing fracture during cyclic loading. Monotonic loading showed that deformation behavior was strongly correlated with pore volume fraction, matching foam theory well; however, fatigue behavior was much more sensitive to local stresses believed to cause crack nucleation.

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http://dx.doi.org/10.1016/j.jmbbm.2014.10.004
1751-6161/

1. Introduction

Poly(*para*-phenylenes) (PPPs) consist of directly linked repeating phenyl units (benzene rings) resulting in strength and stiffness values much greater than other traditional polymeric biomaterials (Morgan et al., 2006; Pei and Friedrich, 2012; Vuorinen et al., 2008). A recent approach in the polymerization of PPPs has been to add side groups to the aromatic backbone, which allows for increased degree of polymerization (Taylor and Samulski, 2000; Percec et al., 1999; Cianga et al., 2002). Therefore, PPPs can now be manufactured in bulk, which has allowed them to be used as a structural engineering material with excellent chemical stability. They are widely considered the stiffest and strongest commercially available thermoplastics, even though their material properties can vary based on the specific side groups present.

To date only a handful of studies have investigated the potential use of PPPs as a biomaterial. A study by Vuorinen et al. (2008) investigated the effect of water absorption on the mechanical properties of PPP. They showed that water absorption was less than 1% after 44 days of soaking and a little-to-no effect was observed on the mechanical properties. Further testing by some of the current authors revealed that the mechanical properties stayed within one standard deviation of dry conditions after soaking in an aqueous environment for over 1 year (Frick et al., 2014). The bulky side groups within the structure of PPPs act as diffusional barriers that prevent water molecules from swelling the polymer (Barnes et al., 1988; Corkhill et al., 1987), resulting in negligible effects on the mechanical properties. In addition to absorption testing, initial cytotoxicity testing of PPP (Frick et al., 2014) shows that it is non-toxic, which was expected due to its chemical inertness.

The mechanical characteristics of the PPP used in this study (PrimoSpire PR-250) were determined in comparison to other common biomedical grade polymers (Frick et al., 2014); it was found that PPP has strength and stiffness much greater than these materials. It was shown that PPP has an average tensile strength of 141 MPa, exceeding that of polyetheretherketone (PEEK) (96 MPa) and high density polyethelene (HDPE) (30 MPa). It was also shown that the average elastic modulus of PPP is approximately 5.0 GPa, far greater than that of PEEK, which ranges from 2.2 to 3.4 GPa (Yakacki, 2013), and HDPE, which is approximately 1.10 GPa (Callister and Rethwisch, 2010). The direct linkage of repeating phenyl units inherent in the microstructure of PPP provides strong anti-rotational biaryl bonds which lead to its exceptional mechanical strength and stiffness. Moreover, the addition of side groups along its backbone causes steric hindrance which further limit chain mobility. Despite its outstanding mechanical behavior, the viability of PPP as a load-bearing biomaterial has been largely uninvestigated.

Porous scaffolds are commonly proposed for orthopedic applications to overcome the failures associated with the loosening of the implant–bone interface (Agrawal and Ray, 2001; Hench, 1991; Rezwan et al., 2006; Converse et al., 2010, 2009; Karageorgiou and Kaplan, 2005; Causa et al., 2006; Kretlow and Mikos, 2007). A porous scaffold could alleviate these problems by allowing for osteointegration, i.e. the physical intermix of bone and implant. The fundamental premise is that during healing the osteoblast cells will penetrate and proliferate into the open-cell porous scaffold. A critical challenge facing orthopedic implants is matching the mechanical properties of trabecular bone. Metal implants tend to have far greater mechanical properties than bone, leading to stress shielding which prevents full healing of the injured site (Bobyn et al., 1992; Bugbee et al., 1997; Nagels et al., 2003; Lewis, 2013). Along with this, bone resorption is common due to the disuse and lack of stimulus for bone maintenance. Porous scaffolds made from traditional polymeric biomaterials lack the strength and stiffness required to match those of trabecular bone. But due to the high bulk modulus of PPP, it can be manufactured at a relatively high porosity, which is necessary for successful osteointegration in vivo (Karageorgiou and Kaplan, 2005), while still matching the mechanical properties of trabecular bone. For example, a recent study found that the elastic modulus of 80 vol% porous PPP was over 120 MPa, while for 70 vol% porous PPP it was approximately 300 MPa (DiRienzo et al., 2014).

The manner in which PPP scaffolds can be manufactured also makes it a viable candidate for orthopedic applications. PPP can be solution cast, hot injection molded, or hot-press sintered into a desired geometry. A manufacturing technique for fabricating porous PPP was established in a previous study (DiRienzo et al., 2014). It was shown that for a large array of porosities and pore sizes, monotonic properties roughly matched those predicted by foam theory (Gibson and Ashby, 1988). Although a range of porous samples have already been monotonically tested, the fatigue characterization of the porous scaffolds was not conducted. Other studies have investigated the mechanical properties of biomedical porous structures and have taken into account the fatigue characteristics (Lewis, 2013; Banhart, 2001; Landy et al., 2013; Lipinski et al., 2013; Yavari et al., 2013). For example, Banhart listed fatigue testing of porous scaffolds as a necessary destructive test in the characterization of potential biomedical materials. Furthermore, the study by Landy et al. emphasized that porous PEEK met the fatigue criteria necessary for its development as a cervical interbody fusion cage. Understanding the fatigue resistance of potential biomaterials for orthopedic applications is of utmost importance due to the cyclic nature of physiological loading (Pruitt, 2005).

While the fatigue behavior of fully dense PPP has been investigated in a previous study (Frick et al., 2014), the fatigue behavior of porous PPP is completely unexplored. Cyclic loading is a common source of failure in polymeric orthopedic devices due to the nature of human motion (Simske et al., 1997; Ganguly et al., 2004; Hartwig and Knaak, 1991; Brillhart and Botsis, 1994; Brillhart et al., 1991; Sobieraj et al., 2010), as such, it has been well documented that this effect must be taken into account when developing a new polymer based biomaterial. The purpose of this study is to further investigate the porous PPP that most closely matches trabecular bone: 75 vol% porous scaffolds with large pore size distribution between 420 and 500 μm (DiRienzo et al., 2014). The large pore size generally agrees with the principles of osteointegration in which pores that are greater than 300 μm are recommended (Karageorgiou and Kaplan, 2005).

The focus of this study was to develop a method that utilizes a combination of micro-computed tomography (μCT) analysis, finite-element analysis (FEA), and experimental testing to understand both monotonic and cyclic behavior as well as