JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 29 (2014) 103–113

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jmbbm

Research Paper

Preparation of three-dimensional braided carbon fiber-reinforced PEEK composites for potential load-bearing bone fixations. Part I. Mechanical properties and cytocompatibility

Honglin Luo[a], Guangyao Xiong[b], Zhiwei Yang[a], Sudha R Raman[c], Qiuping Li[b], Chunying Ma[b], Deying Li[b], Zheren Wang[a], Yizao Wan[a,*]

[a]School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, China
[b]School of Mechanical and Electrical Engineering, East China Jiaotong University, Nanchang, Jiangxi 330013, China
[c]Department of Community and Family Medicine, Duke University, NC, USA

ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form
27 August 2013
Accepted 1 September 2013
Available online 17 September 2013

Keywords:
Carbon fiber
Polyetheretherketone
3-Dimensional reinforcement
Porosity
Surface treatments

ABSTRACT

In this study, we focused on fabrication and characterization of three-dimensional carbon fiber-reinforced polyetheretherketone ($C_{3\text{-}D}$/PEEK) composites for orthopedic applications. We found that pre-heating of 3-D fabrics before hot-pressing could eliminate pores in the composites prepared by 3-D co-braiding and hot-pressing techniques. The manufacturing process and the processing variables were studied and optimum parameters were obtained. Moreover, the carbon fibers were surface treated by the anodic oxidization and its effect on mechanical properties of the composites was determined. Preliminary cell studies with mouse osteoblast cells were also performed to examine the cytocompatibility of the composites. Feasibility of the $C_{3\text{-}D}$/PEEK composites as load-bearing bone fixation materials was evaluated. Results suggest that the $C_{3\text{-}D}$/PEEK composites show good promising as load-bearing bone fixations.

1. Introduction

Fiber reinforced polymer matrix composites were initially used in the aerospace industry, where critical importance is placed on the use of lightweight materials. Decades later, fibrous composites found applications in other areas such as automobiles, infrastructure and biomaterials in light of their good environmental stability, moldability and damage resistance. Traditional thermosets took the lead as matrix materials for fibrous composites as they are easy to work with, and resistant to solvents and corrosion as compared to thermoplastics. Advantages of thermoplastic composites make them attractive in many applications including biomedical areas (Brockett et al., 2012; Morrison et al., 1995; Williams et al., 1987). These advantages include an increased impact resistance as compared to thermoset composites, the ability to reshape and reform when heated during surgery and the ability to be recycled at the end of life. However, one

*Corresponding author. Tel./fax: +86 22 8789 8601.
E-mail addresses: yzwantju@126.com, yzwan@tju.edu.cn (Y. Wan).

1751-6161/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jmbbm.2013.09.003

of the biggest obstacles to the manufacture of thermoplastic composites is the difficulty impregnating the reinforcing fibers due to the matrix material's high viscosity in its melted state. Accordingly, initial thermoplastic composites were reinforced with discontinuous (chopped) fibers like carbon fibers (Brown et al., 1990; Williams et al., 1987). However, the strength of the resulting material was not comparable to continuous fiber reinforced composites. The manufacturing process of continuous fiber thermoplastic composites, including unidirectional, laminate, two-dimensional (2-D) and three-dimensional (3-D) textiles, is complex and far different from traditional thermoset composite manufacturing. Of these continuous fiber types, manufacture of 3-D textile thermoplastic composite is the most difficult since impregnation of molten matrix into the inner part is hindered by the existence of the through-thickness reinforcements. Generally, resin transfer molding (RTM) is widely employed to manufacture thermoset-based 3-D composites like epoxy and unsaturated polyester. However, RTM has rarely been used to prepare 3-D thermoplastic-based composites since almost no thermoplastic material can meet the stringent rheological requirements. An exception can be found in our previous report (Wang et al., 2003) where 3-D braided carbon fiber and Kevlar fiber reinforced monomer casting (MC) nylon composites were fabricated by an RTM-aided vacuum solution impregnation plus an in situ anionic polymerization technique, making use of the low viscosity of the monomer of MC nylon. However, this technique cannot be used for other polymers. To this end, much effort has been made to find novel effective techniques to prepare fibrous 3-D composites.

Currently, the post-impregnation is the most feasible process for 3-D thermoplastic composites, as long as the polymers are available in film (the most suitable), fiber or powder forms (Kuo and Fang, 2000). The process is divided into two steps: In step one, the polymeric fibers are mixed with reinforcing fibers to form a commingled bundle. In step two, the commingled bundle is heated at the temperature higher than the melting point of polymeric fibers to allow for the impregnation of the reinforcing fibers. Examples can be found in references for carbon or graphite fiber-reinforced polyetheretherketone (PEEK) composites (Chu et al., 1992). The use of PEEK is based upon the fact that PEEK has superior mechanical and biological properties as compared to conventional thermoplastics. Detailed review on the use of PEEK biomaterials in trauma, orthopedic, and spinal implants can be found elsewhere (Kurtz and Devine, 2007). The combination of carbon fiber and PEEK further improves the mechanical properties of PEEK. Both pure and carbon fiber-reinforced PEEK have been used in a wide range of applications in the automotive, aerospace, electronics, chemical processing industries, and medicine. For example, continuous carbon fiber-PEEK composites have been used as implant materials in orthopedic medicine (Steinberg et al., 2013). The use of 2-D braided and knitted carbon fiber-PEEK composites as bone plates has also been reported (Fujihara et al., 2003, 2004).

When fibrous thermoplastic composites are used for orthopedic bone fixation, 3-D braided composites possess some advantages when compared with short, continuous and 2-D fabrics reinforced composites. These include balanced properties in various directions, higher damage and delamination tolerances, and better impact and fatigue properties than 2-D composites (Chou et al., 1992; Takatoya and Susuki, 2005). Further advantages are their ability to reshape to match the geometry of human bones and to control stiffness, therefore creating a state of stress in bones that is close to physiological levels. Moreover, the increased concern for metallosis associated with metal implants (Mohammed and Cnudde, 2012; Romesburg et al., 2010) makes the composites more attractive. However, the use of 3-D braided carbon fiber-reinforced PEEK ($C_{3\text{-}D}$/PEEK) for load-bearing bone fixations has not been previously reported. Furthermore, the manufacturing process of $C_{3\text{-}D}$/PEEK composites has not been investigated in detail and the surface treatment of carbon fibers has not been performed.

The purpose of this study was to (a) investigate the manufacturing process (i.e., hot-pressing) and the effect of the processing parameters (temperature and pressure) on the microstructure and properties of $C_{3\text{-}D}$/PEEK composites, (b) to determine the effects of surface treatment of 3-D braided carbon fiber and its volume fraction on the performance of the composites, (c) to examine the cell compatibility of the composites, and (d) to evaluate the feasibility of the $C_{3\text{-}D}$/PEEK composites for use in load-bearing bone fixation.

2. Materials and methods

2.1. Fabrics preparation

The T300 carbon fiber used in this study was supplied by Weihai Guangwei Composites Co., Ltd., Shandong, China. The carbon fibers were 3 k fiber tow with a tensile strength of 3350 MPa and modulus of 230 GPa. The 550F30 PEEK multi-filament fiber yarn was purchased from ZYEX Ltd., Stonehouse, United Kingdom. The PEEK fibers had a density of 1.3 g/cm^3, a melting point of 334 °C and a glass transition temperature of 143 °C.

The preforms, 3-D five directional fabrics with a braiding angle of 25°, nominal width of 12 mm and thickness of 4 mm were prepared by the Nanjing Fiberglass R&D Institute, Nanjing, China. PEEK fibers and carbon fibers were co-braided to make 3-D braided hybrid fabrics. The braiding process was described elsewhere (Wan et al., 2007b). Briefly, the hybrid fabrics used in the 3-D braided preforms were constructed by the orthogonal interlacing of two sets of yarns–braiders and axials to form a fully integrated structure. Four hybrid fabrics with varying carbon fiber volume fractions (0, 18, 36, and 54%) were prepared in this study. Typical photos of the four fabrics are displayed in Fig. 1.

2.2. Surface treatment of fabrics

In order to improve fiber–matrix adhesion, some 3-D hybrid fabrics were surface treated before consolidation. An anodic oxidization process was employed according to previous studies (Wan et al., 2006; Yumitori, 1996). Hybrid fabrics were first immersed in 5% $(NH_4)_2HPO_4$ solution and boiled for an hour, and then rinsed several times with distilled water, and finally dried at 80 °C for 10 h.