Materials and Design 116 (2017) 171–175

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Porous polyether ether ketone: A candidate for hard tissue implant materials

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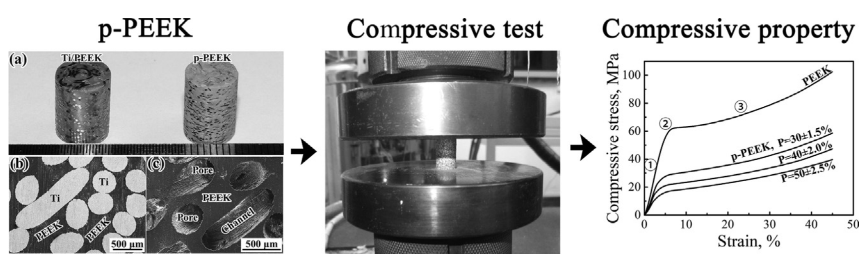
HIGHLIGHTS

- This p-PEEK material has a novel inner porous structure.
- The pore size and porosity of this p-PEEK material can be easily controlled.
- The elastic modulus of this p-PEEK material reached the floor level of cortical bone.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form 30 November 2016
Accepted 4 December 2016
Available online 07 December 2016

Keywords:
PEEK
Porous material
Biomedical material
Mechanical property
Implant

ABSTRACT

A porous polyether ether ketone (p-PEEK) was fabricated by firstly preparing titanium/PEEK composite (Ti/PEEK) (die casting) and then removing titanium wire (acid etching). The pores in p-PEEK can provide channels for bone cells ingrowth and body fluid transmission. The pore size and porosity of p-PEEK can be tailored by adjusting the diameter and volume fraction of titanium wire that was used in the preparation process. The average cell wall thicknesses of p-PEEK with porosities of 30 ± 1.5%, 40 ± 2.0% and 50 ± 2.5% were 326.4 μm, 297.6 μm and 255.4 μm, respectively. The compressive yield strengths and the elastic moduli of p-PEEK with porosities ranged of 30%–50% were 28–16 MPa and 5.5–3.0 GPa, respectively. The elastic modulus of p-PEEK reached the floor level of cortical bone (3.0–30.0 GPa). The relationship of the relative elastic moduli to the relative densities of p-PEEK conformed to the Gibson-Ashby model. This porous PEEK is expected to be a candidate for hard tissue implant materials.

1. Introduction

Polyether ether ketone (PEEK) was invented by DuPont (USA) and the patent granted in 1962. PEEK as biomedical material has the advantages of favorable mechanical properties, perfect chemical stability, irradiation sterilization resistant, non-cytotoxic and non-sensitization [1–4]. Stawarczyk et al. [5] have studied the fracture load of PEEK three-unit fixed dental prostheses (FDPs), and found that the PEEK three-unit FDPs showed a mean fracture load of 1383 N with a plastic deformation starting approximately at 1200 N. The result indicated that the strength of PEEK met the mechanical requirement of implant applications. Kim et al. [6] have studied the fatigue limits of glass fiber-reinforced PEEK (GFR-PEEK) dental implants. The result showed that the fatigue limits of GFR-PEEK were 310 N, which was performed according to ISO 14801. Moriarty et al. [7] have investigated *Staphylococcus aureus* and *Staphylococcus epidermidis* adhesion to injection moulded and machined PEEK, and found that the rougher machined PEEK had a

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http://dx.doi.org/10.1016/j.matdes.2016.12.012
0264-1275/

significantly greater number of adherent bacteria compared to injection moulded PEEK. What's more, the PEEK has been successful application of spinal intervertebral fusion [8].

However, as a hard tissue implant material, a drawback of PEEK is its inert property, PEEK fails to integrate well with bone [9–12]. Material modification is a way to improve the bioactivity of PEEK. Barkarmo et al. [13] have studied the osseointegration of surface-modified PEEK implants in rabbit bone. The PEEK implants coated with nanocrystalline hydroxyapatite (nano-HA) showed better osseointegration than the uncoated PEEK implants. Using MG-63 cell and beagle dog, Deng et al. [14] have studied the in vitro and in vivo bioactivity of nano-TiO_2/PEEK bioactive composite that was fabricated by powder mixing and compression moulding methods, and found that the nano-TiO_2 significantly improved the bioactivity of PEEK. Rupprecht et al. [15] have studied the effect of β-TCP filled PEEK on osteoblast cell proliferation in vitro. The results showed that β-TCP filled PEEK showed concentration independent decrease of cell proliferation compared to the unfilled PEEK. Cook and Rust-Dawicki [16] have placed titanium-coated and uncoated PEEK in the femurs of mongrel dogs, and found the titanium-coated specimens had significantly higher percentages of bone contact than the uncoated specimens. As a hard tissue implant material, the weak mechanical interlocking between PEEK implant and bone may lead to implant failure. Research and development of porous PEEK is a way to solve this problem. Open pores in biomedical materials can provide channels for bone cells ingrowth and body fluid transmission, which is beneficial for prosthesis fixation [17–19]. Kennedy and Siddiq [20] have reported a porous PEEK manufactured by a novel powder route using near-spherical salt bead porogens. This porous PEEK has excellent repeatability and homogeneity of density, and has more uniform pore and strut sizes. The imperfection of this porous PEEK is its mechanical properties (compression yield stress > 1 MPa and stiffness > 30 MPa) did not achieve the requirement of load-bearing biomedical material.

In this study, a porous PEEK was fabricated. The pore size and porosity of the p-PEEK can be tailored by adjusting the diameter and volume fraction of titanium wire that was used in the preparation process. The cell wall thickness distributions of p-PEEK with different porosities were analyzed, and the compressive performances of p-PEEK with different porosities were tested. This study can provide valuable data for the applications of this material as a hard tissue implant material.

2. Materials and methods

2.1. Materials

Commercial pure titanium wire (99.9% purity, 0.40 mm in diameter, 4.51 g/cm^3, from Shanghai Zu Li Company, Shanghai, China) and PEEK 450G (from Xing Ye Sheng Plastic Material co., LTD, Shenzhen, China) were used as raw materials. The preparation process included three steps: firstly preparation of the entangled porous titanium (p-Ti) (by mould pressing), then infiltration of molten PEEK into the p-Ti to form Ti/PEEK composite (by die casting, 340 °C), and finally removal of titanium wire to form p-PEEK (by chemical etching, 10% hydrofluoric acid, room temperature, 1-4 h).

The porosity of the p-PEEK can be tailored by adjusting the volume fraction of titanium wire in Ti/PEEK composite. The volume fraction of titanium wire was controlled by adjusting the weight of titanium wire that was used. It was calculated by the following equation [21]:

$$m_{Ti} = V \times \psi_{Ti} \times \rho_{Ti} \quad (1)$$

where m_{Ti} indicates the weight of titanium wire, V indicates the volume of Ti/PEEK sample, ψ_{Ti} indicates the volume fraction of titanium wire in Ti/PEEK composite and ρ_{Ti} indicates the density of titanium wire.

The shape of pores in p-PEEK was copied from the shape of titanium wire in as-prepared p-Ti. The diameter of pores in p-PEEK was approximately equal to the diameter of titanium wire. The most suitable pore size for bone cell growth in is 100–500 μm [17,18,22]. In this study, titanium wire with diameter of 400 μm was used. So the diameter of pores in the p-PEEK was 400 μm. Porous PEEK materials with three porosities (30 ± 1.5%, 40 ± 2.0% and 50 ± 2.5%) were prepared in this study. Specimens with dimensions of Ø10 × 3 mm and Ø8 × 12 mm were prepared respectively for morphology analysis and compressive test.

2.2. Morphology analysis

The morphologies of p-PEEK samples were observed by optical microscope and scanning electron microscope (SEM). The cell wall thickness distributions of p-PEEK with different porosities were statistically analyzed by using the commercial Image Pro Plus software. Ten samples were analyzed and 400 data points were collected for each group.

2.3. Compression tests

The compression tests were conducted on a ZWICK AG-100KN testing machine. The tests were conducted at a crosshead speed of 1 mm/min. Three samples were tested for each group. The average of three measurements was taken as the report value.

In order to evaluate the mechanical properties of p-PEEK, the yield strengths and elastic moduli were estimated according to the stress–strain curves. The schematic diagram of calculation methods was shown in Fig. 1. As described in the previous paper [23], the yield strength was estimated by extending the elastic curve and the pseudo-platform curve, and the cross point was defined as the yield point. The elastic moduli of p-PEEK were calculated according to the slopes of elastic stage of the stress–strain curves. It can be calculated by the following equation:

$$E = \delta/\varepsilon = (y_1 - y_2)/(x_1 - x_2) \quad (2)$$

where σ is the engineering stress and ε is the engineering strain.

All the elastic moduli of the materials in this study were calibrated by Kalidindi's method [24]. The elastic moduli were calibrated by subtracting the compliance that determined by comparing the difference between the measured and theoretical load–displacement relationships.

3. Results and discussion

3.1. Morphological characterization of the p-PEEK

The morphologies of Ti/PEEK composite sample and p-PEEK sample were shown in Fig. 2a. The cross-section image of Ti/PEEK composite with titanium wire volume fraction of 40 ± 2.0% and wire diameter of 400 μm was shown in Fig. 2b. The PEEK was filled into the pores of p-Ti to form the Ti/PEEK composite. The cross-section image of p-PEEK

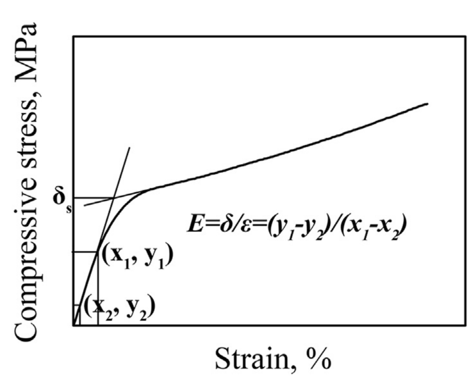

Fig. 1. Schematic diagram of calculation methods of yielding strengths and elastic moduli of the p-PEEK.