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Flexural Mechanical Properties of Functional Gradient Hydroxyapatite Reinforced Polyetheretherketone Biocomposites

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Functional gradient hydroxyapatite reinforced polyetheretherketone is one of the most promising orthopedic implant biomaterials. In this study, functional gradient hydroxyapatite reinforced polyetheretherketone biocomposites were prepared by layer-by-layer method with the incorporation of hot press molding technology. Studies on the flexural mechanical properties of the functional gradient biocomposites revealed that the flexural stress–stain behavior of the biocomposites presented linear elastic characteristics. The fracture mechanism of the functional gradient biocomposites was predominated by brittle rupture. Furthermore, both flexural strength and break strain of the functional gradient HA/PEEK biocomposites obviously decreased with the rise of the total HA content. The effect of hydroxyapatite concentration difference between adjacent layers (HCDBAL) on the flexural strength obviously relied on the level of HCDBAL and total HA content in the functional gradient HA/PEEK biocomposites. The higher the total HA content in the functional gradient biocomposites is, the less the influence degree of HCDBAL on the flexural strength is. Moreover, total HA content and HCDBAL played synergistic influence on the flexural modulus of the functional gradient HA/PEEK biocomposites.

1. Introduction

Polyetheretherketone (PEEK) is one of the most high-performance thermoplastic materials, which is a semi-crystalline thermoplastic polymer with an approximate crystallinity of 30%–35%[1,2]. PEEK has been used in a wide range of applications due to its outstanding properties such as superior mechanical properties, excellent wear-resistance, environmental resistance and thermal stability[3–5]. Especially, PEEK and PEEK composites used as implant materials for replacing and repairing hard tissues of human body have attracted increasing attention because of their excellent mechanical and biocompatibility properties[6–8]. Compared with traditional orthopedic implants such as metallic and ceramic implants, one of the benefits of PEEK based composites is that they could overcome the disadvantages of metallic and ceramic implants currently adopted in orthopedic application. It is well known that the modulus of the traditional orthopedic alloys and ceramic used in hard tissue reconstruction is 10–20 times greater than that of the bone. Thus, it will inevitably be a modulus of the implant mismatch with that of natural bone, thereby producing stress shielding effect, which would lead to the aseptic loosening of implants and bone loss. Moreover, many studies revealed that the electrochemical reaction of the metal alloy joint implants would occur and thus release metal ions into the natural tissue. The toxicity of metal ions released from metal joint still remains controversial[9–11]. Recently, PEEK and its composites have been widely used in orthopedic applications including the femoral component of total hip replacements, bone anchors, cervical total disc arthroplasty, intervertebral cages, dental implant systems and fracture fixation plates[12–14].

However, the mechanical properties of PEEK used in most load-bearing orthopedic implant should be further improved. Moreover, the traditional methods of stabilizing the prosthesis such as bone cement fixation are mostly substituted by bioactive fixation. The bioactive fixation technology requires prosthesis with good biocompatibility as well as excellent bioactivity. Lots of efforts have been devoted to improving the mechanical and bioactive properties of polyetheretherketone[15,16]. One of the most effective methods is to incorporate bioactive ceramics such as tricaclium phosphate, hydroxyapatite and bioactive glass-ceramics with PEEK polymer[17,18]. It should be noted that hydroxyapatite is an excellent candidate reinforcement and bioactive component for biocomposites on account of its similar constituent as that of inorganic component in natural bone and outstanding bioactive characteristics. Polymeric implant combination with HA promotes new bone growth from the existing bony walls (osteoconductive) onto it, thus stabilizing the prosthesis within a short period of time. In recent years, hydroxyapatite reinforced polyetheretherketone has been demonstrated to show

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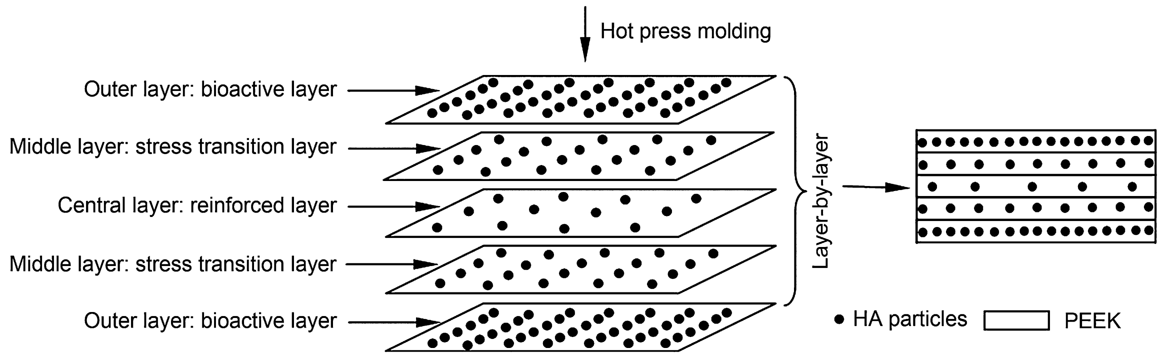

Fig. 1. Schematic diagram of the functional gradient HA/PEEK biocomposites.

excellent bioactive performance[19]. Most of studies verified that the mechanical strength of PEEK can be importantly improved by the addition of certain content of hydroxyapatite particles in the PEEK matrix[20,21]. On the other hand, it is necessary to incorporate a larger amount of HA particles into the PEEK matrix to improve the bioactive properties of the composites. However, the excess of HA particles generally results in the brittleness of the composites accompanied with a significant deterioration of mechanical strength. Thus, there is conflict in simultaneously optimizing the mechanical and bioactive properties of hydroxyapatite reinforced polyetheretherketone biocomposites.

The functional gradient design is an effective method to solve the conflict between mechanical and bioactive performances of the HA/PEEK biocomposites. Here, we selected hydroxyapatite particles as bioactive constituents as well as reinforcement and the polyetheretherketone as matrix to prepare functional gradient HA/PEEK biocomposites. The functional gradient HA/PEEK biocomposite is composed of symmetrical five layers, which are respectively denoted as outer layer, middle layer and central layer (Fig. 1). The HA particle content in the functional gradient biocomposites presents increasing trend from central to the outer layer. The outer layer with the highest HA content endows the functional gradient biocomposites with outstanding bioactivity. The central layer with lowest HA content offers the functional gradient biocomposites appropriate mechanical strength and suitable ductility. The middle layer with moderate HA content makes the stress effectively transfer among the layers in the functional biocomposites. According to this design, the functional gradient HA/PEEK biocomposites with an outer layer containing high HA content and inner layer containing low HA contents would realize the simultaneous optimization on mechanical and bioactive properties of the biocomposites by altering the layer HA content in the composites.

Currently, many works have attempted to improve the mechanical and bioactive properties of polyetheretherketone. However, it is a pending question to simultaneously optimize the mechanical and bioactive properties of PEEK. According to the authors' knowledge, little attention has been devoted to solve the conflict between mechanical and bioactive properties of PEEK material through functional gradient design. The purpose of this initial investigation was to estimate the mechanical properties of the functional gradient HA/PEEK biocomposites under bending load. The influence of various factors on the flexural mechanical properties was investigated.

2. Experimental

2.1. Materials

Polyetheretherketone powder with the average diameter of 50 μm (VICTREX® PEEK, 450PF) was manufactured by VICTREX PIC, U.K. and purchased from SCM Industrial Chemical Co., Ltd. Calcium hydroxide ($Ca(OH)_2$) and phosphoric acid (H_3PO_4) were produced and purchased from Siopharm Chemical Reagent Co., Ltd. All the chemical reagents were of analytical grade.

2.2. Preparation of functional gradient HA/PEEK biocomposites

In order to fabricate functional gradient HA/PEEK biocomposites, the HA–PEEK composite powder were first prepared by in-situ synthesis process according to our previous work[22]. The main processing schedule is described as follows. First, a certain amount of $Ca(OH)_2$ and PEEK powder was mixed in distilled water at 80 °C for 30–50 min by an electric agitator. Then H_3PO_4 solution was slowly added into $Ca(OH)_2$ and PEEK solution at 90 °C under electric agitator stirring. The amount of H_3PO_4 to be added was controlled with Ca/P molar ratio of 1.67. After $Ca(OH)_2$ and H_3PO_4 had thoroughly reacted, the solution was aged at 80 °C for 10–12 h. Subsequently, the solution was rinsed and filtered repeatedly using distilled water until the pH value of the filtrate was close to 7. Finally, the residue was dried in an oven at 120 °C to constant weight. According to this procedure, HA–PEEK composite powder with various HA contents were harvested.

Functional gradient HA/PEEK biocomposites were prepared by layer-by-layer casting method with the incorporation of hot pressure molding technology. First, HA–PEEK composite powder with different HA concentrations was symmetrically stacked into five layers in a steel die with rectangular shape. The HA concentration in the HA–PEEK composite powder presents an increasing trend from central to the outer layer along with the thickness direction. The mass of the HA–PEEK composite powder in the central layer is about twice the mass of the HA–PEEK composite powder in the middle and outer layers, respectively. Then the samples were heated with thermoforming equipment from room temperature to 380–390 °C and held there for 30–50 min to ensure that the PEEK in the composite powder was completely melted. Subsequently, 4–8 MPa pressure was applied to the sample and the pressure was kept for 15 min at temperature of 380–390 °C. After then, the temperature was lowered to 300 °C and then the pressure was removed. Finally, the sample was cooled down in air to room temperature. According to this process schedule, functional gradient HA/PEEK biocomposites could be fabricated. Fig. 1 illustrates the schematic diagram of functional gradient HA/PEEK biocomposites.

2.3. Flexural mechanical property measurement

A three-point bending test was employed to evaluate the flexural properties such as flexural strength, flexural strain and modulus of functional gradient HA/PEEK biocomposites on mechanical test equipment (Model: CMT-5105, Shenzhen SANS Material Detection