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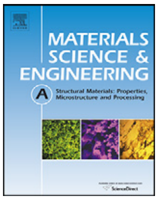

Characterization of polyetheretherketone–hydroxyapatite nanocomposite materials

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ABSTRACT

Polyetheretherketone–hydroxyapatite nanocomposite materials are investigated for the purpose of improving the bonding between polyetheretherketone (PEEK) matrix and hydroxyapatite (HA) fillers since their debonding deteriorates the otherwise superior antifatigue properties of PEEK materials. The nanocomposites are successfully produced by incorporating lab-prepared HA nanoparticles, up to 15.0 vol%, to PEEK matrix via a compounding and injection molding process. The microstructures of the composite samples are observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystallization and phase structure of the composites are examined by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements. The mechanical properties of the composites are evaluated, and their tensile strength reaches 98 MPa at 5.0 vol% HA. Most importantly the study suggests that there is no debonding occurring between the well-dispersed HA nanoparticles and PEEK matrix, which provides a promising way to overcome the debonding issue of the PEEK–HA composites.

1. Introduction

Research interests have recently arisen on the biological applications of polyetheretherketone (PEEK) polymers because they have strong resistance to hydrolysis and excellent chemical stability under UV irradiation used for antibacterial treatment in conjunction with their outstanding mechanical properties and thermal stability [1]. For example, the PEEK application for the cervical disc disease has been evaluated in a group of 80 patients, showing that the PEEK devices can facilitate the stability and space maintenance during the cervical fusions [2]. The PEEK–carbon fiber composite plates are found to be suitable for forearm treatment and femur or tibia fixation [3]. Although these results indicate that PEEK materials have good biocompatibility, their bioactivity is reported to be similar to that of bioinert titanium alloy [4]. To improve the bioactivity of PEEK materials, the PEEK–hydroxyapatite (HA) composite materials were produced through incorporating microsize HA particles to PEEK matrix [5]. These PEEK–HA composites, indeed, exhibit reasonably good bioactive properties [6] and the bioactivity of the composites is enhanced with increasing HA content [7], but, at the same time, the tensile strength and the strain to failure of the materials decrease substantially [5]. Scanning electron micrographs of the fracture surfaces of the PEEK–HA composites reveal that the interfacial debonding between PEEK matrix and HA fillers is common with ductile failure [6]. The weakened interfaces have been found to deteriorate the otherwise superior anti-fatigue properties of PEEK materials [6,8]. The fatigue properties of the biomaterials are critical for long term biological applications, such as implants, and therefore the further research is needed to improve the adhesion of HA fillers to PEEK matrix, as suggested by Kurtz and Devine [1]. Scanning electron micrographs presented in some recent studies [9,10] exhibit that the bonding between the microsized HA fillers and PEEK matrix appears to be fairly strong in the composites prepared by a similar processing to a previous study [5], but the reasons accounting for the difference between the studies of Ref. [6] and Refs. [9,10] remain unexamined.

On the other hand, the inorganic nanoparticles, such as nano-Al_2O_3 and nano-SiO_2, have been known to enhance the bonding between nanofillers and polymeric matrix and to improve the mechanical properties of the nanocomposite materials [11,12]. Therefore, it is expected that the bioactive nanofillers, e.g., hydroxyapatite nanoparticles, may play a similar role in strengthening the bonding between HA nanofillers and PEEK matrix, consequently producing a nanocomposite material with both excellent mechanical properties and high bioactivity. However, until the present time, few studies have been reported in this field. The aim of the present

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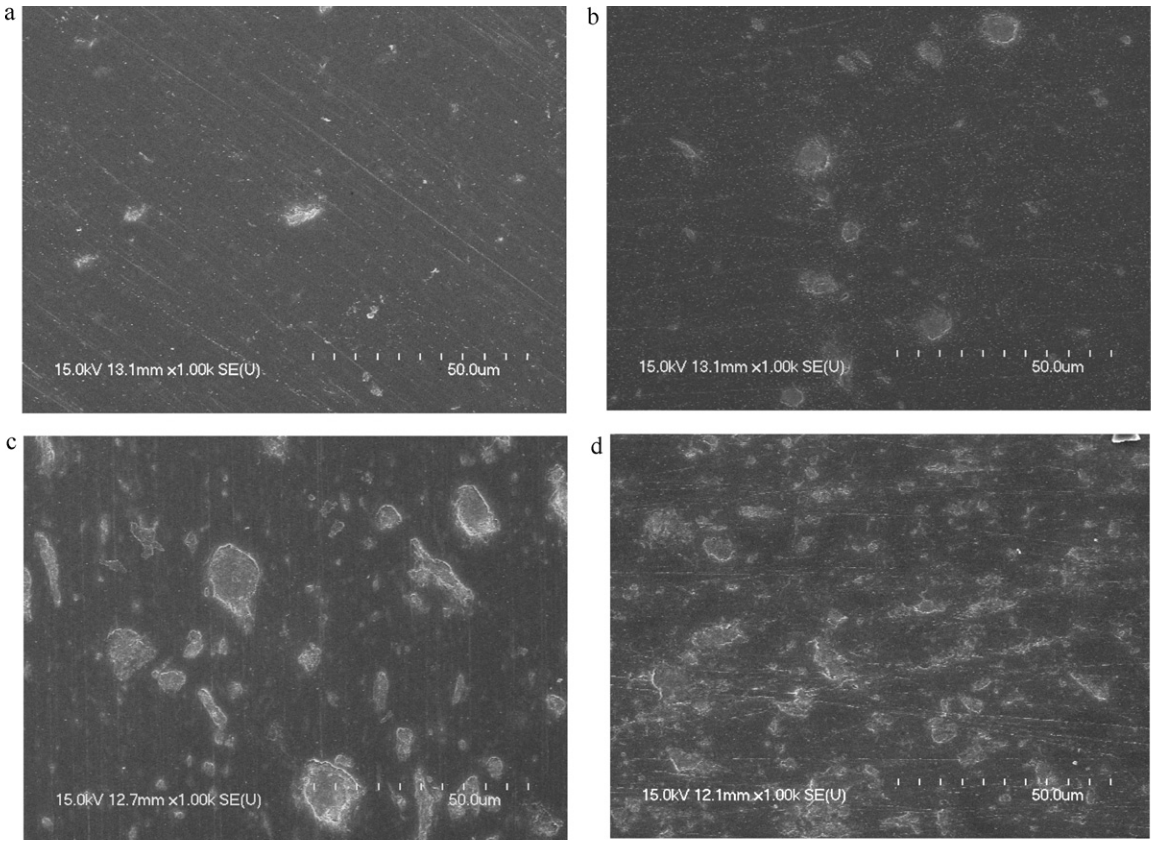

Fig. 1. SEM micrographs of PEEK–HA nanocomposites with (a) 2.0 vol% HA; (b) 5.0 vol% HA; (c) 10.0 vol% HA; and (d) 15.0 vol% HA.

study is therefore to investigate PEEK nanocomposite materials reinforced by HA nanoparticles.

2. Experimental

2.1. Materials

The hydroxyapatite nanoparticles were prepared in the laboratory by a hydrothermal process described in Ref. [13]. The well-crystallized HA nanoparticles was monodispersed without identifiable hard agglomerates and its size was within nanometer domain with a width ranging from 20 to 30 nm and a length from 60 to 100 nm.

The medium viscosity grade PEEK polymer (380G, Jidaxincai, China) was used as the matrix material. The PEEK–HA nanocomposite specimens with HA contents up to 15 vol% were prepared via a compounding and injection molding process. The PEEK powder and the lab-prepared HA nanoparticles were compounded in a high speed ball mill at a mixing speed of 400 rpm for 2 h, and then the mixtures were dried in air at 160 °C for 24 h. The specimens with difference shapes, according to the measurement requirements, were produced on an injection molding machine with an injecting temperature between 360 and 380 °C and a molding temperature between 200 and 220 °C, depending on HA content. The samples for the strength and micro-hardness measurements were further annealed at 200 °C for 1 h.

2.2. Characterization

The influence of HA content on the thermal behavior of the PEEK–HA nanocomposites prepared by the injection process was studied by a differential scanning calorimeter (DSC, TA Instruments). The samples were firstly heated to 410 °C at a heating rate of 10 °C/min in a nitrogen atmosphere, and held there for 5 min to remove the previous thermal history, and then cooled to 50 °C at a cooling rate of 10 °C/min. The samples were subsequently reheated from 50 to 410 °C at 10 °C/min. The X-ray diffractometer (Bruker AXS, D8 Advance Diffractometer) with a monochromatic Cu Kα radiation source was employed to investigate phase structures of the composite materials. The ultimate tensile strengths and the break elongation of the dumbbell-shaped specimens were measured in accordance with ASTM D638 for tensile testing by an Instron IX Material Testing System at room temperature. A Shimadzu HMV-2000 Vickers micro-hardness tester was employed to evaluate the micro-hardness of the samples.

Scanning electron microscopy with energy dispersive X-ray spectra (EDX) (SEM, Hitachi S-4700) was used to examine the composition and microstructure of the nanocomposite specimens. Prior to measurements, the specimens were first polished, and then coated with a thin layer of gold using a gold sputter coater to minimize charging effects. The distribution of HA nanoparticles in the composite materials was also observed by TEM (JEM 100CX, Jeol, Japan).

3. Results and discussion

3.1. Preparation of PEEK–HA nanocomposites

SEM micrographs of the specimens containing different HA contents are given in Fig. 1, showing some voids on the polished surface of specimens, which may be caused by the loss of a fraction of HA agglomerates during the process of sample polishing. The remains