JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 49 (2015) 1–11

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jmbbm

Research Paper

Mechanical, thermal and bio-compatibility studies of PAEK-hydroxyapatite nanocomposites

*Pratik Roy, R.R.N. Sailaja**

The Energy and Resources Institute (TERI), SRC, Bangalore 560071, India

ARTICLE INFO

Article history:
Received 14 January 2015
Received in revised form
17 April 2015
Accepted 20 April 2015
Available online 28 April 2015

Keywords:
Poly(aryl ether) ketone
Poly(dimethyl siloxane)
Nanohydroxyapatite
Mechanical properties

ABSTRACT

In this study high performance bone analogue has been developed using poly(aryl ether) ketone, poly(dimethyl siloxane) and reinforced with nanohydroxyapatite as biocompatible filler. Compressive, tensile and flexural properties have shown sustained improvement up to 7% of nanohydroxyapatite loading. The mechanical properties were further analyzed using micromechanical theories for good interfacial adhesion between matrix and filler. The composites are cytocompatible and revealed multiple layers of apatite formation in simulated body fluid. The thickness of apatite layer increased with increase in nanohydroxyapatite loading in the composite. Poly(dimethyl siloxane) has been grafted with phosphate group to enhance compatibility with nanohydroxyapatite. Nanohydroxyapatite has been treated with silane to enhance compatibility and facilitate dispersion in the matrix as observed through transmission electron microscopy, scanning electron microscopy and X-Ray diffraction studies.

1. Introduction

Hydroxyapatite is well known for its high biocompatibility and osteoconductivity. It is similar in chemical structure to the inorganic composition of human bone and thus it is often used in bone reconstruction, maxillofacial and periodontal surgery (Hench, 1998). However, hydroxyapatite alone has certain shortcomings such as poor load bearing properties, difficulty in casting into the desired shape and its tendency to migrate from the implanted sites (Nikpour et al., 2012; Yamaguchi et al., 2001). Polymers have been used to improve the mechanical properties of hydroxyapatite (compressive strength, Young's modulus and fracture toughness). Bioactive polymer composites can be prepared by incorporating bioactive hydroxyapatite fillers in biocompatible or bio-inert matrices, which is necessary for promoting bone regeneration and forming strong interfacial fixation between host tissue and implant (Utzschneider et al., 2010). Composites with hydroxyapatite and a polymer such as high-density polyethylene (HDPE), poly(methyl methacrylate) (PMMA), Polyactive™, polylactic acid (PLLA), polyhydroxybutyrate (PHB) and polyether ether ketone (PEEK) have been used as potential materials for bone tissue replacement (Abu Bakar et al., 2003). Among them, special attention has been focused on the biocomposites with the PEEK matrix. It has superior mechanical and chemical properties, such as high strength, good wear resistance, fracture toughness, fatigue properties along with excellent chemical resistance (Ha et al., 1997). PEEK can replace metals in load-bearing orthopaedic and spinal

---

*Corresponding author. Tel: +91 80 25356590.
E-mail address: sailaja.bhattacharya@gmail.com (R.R.N. Sailaja).

http://dx.doi.org/10.1016/j.jmbbm.2015.04.022
1751-6161/© 2015 Elsevier Ltd. All rights reserved.

implants due to biocompatibility, safety and biomechanical properties (Sagomonyants et al., 2008). They are also considered as the ideal material to apply in spinal cages and artificial joints (Williams, 2008). Moreover, PEEK has an elastic modulus which is in the same range as cortical bone which enables improved transfer of osteogenic strains to the bone tissue (Skinner, 1988). Radiolucency of PEEK enables improved post-operative assessment of fusion by eliminating radiographic artifacts caused by using metallic scaffolds and implants (Eck et al., 2000; Diedrich et al., 2001). Abu Bakar et al. (2003) developed PEEK-hydoxyapatite composites as an alternative material for load-bearing orthopaedic applications and demonstrated that they possess sound bioactive properties. Yu et al. (2005) suggested that bioactivity of the composite increases with the increase in hydroxyapatite content. However, the tensile strength and the strain to failure of the composites decreased substantially with the addition of hydroxyapatite particles (Abu Bakar et al., 2003). Gabriel et al. (2006) prepared compression-molded PEEK composite reinforced with hydroxyapatite whiskers. Increased hydroxyapatite whisker reinforcement resulted in increased elastic modulus, but decreased ultimate tensile strength, strain-to-failure and work-to-failure. There are a couple of implantable devices based on PEEK and hydroxyapatite available in the market such as Zeniva® by Solvay Plastics and hydroxyapatite coating on PEEK (Accentus Medical) in order to improve its bioactivity.

In the present study, we have developed a high performance polyaryl ether ketone (PAEK) based nanocomposites with nano-hydroxyapatite (nHA), polydimethyl siloxane (PDMS) and reinforced with nano carbon fibre (NCF). Dispersion of filler particles can improve interfacial adhesion and this leads to better stress sharing which in turn enhances the load bearing properties of the nanocomposites. Thus, in order to facilitate better dispersion and interfacial adhesion between the components of the composites, phosphate functionalization of PDMS and silane treatment of nHA and NCF has been carried out. Therefore, mechanical and thermal properties of these composites loaded with varied amounts of nHA have been studied. The cytotoxicity of the composite material and apatite formation in simulated body fluid (SBF) has also been examined.

2. Experimental

2.1. Materials

PAEK (M_W=133,100) powder used in this study was kindly gifted by Gharda Chemicals, Mumbai (India). PDMS (M_W=1198), 2-methacryloxy Ethyl Phosphate (MAEP), 3-aminopropyl triethoxy silane (APTS) and NCF used in this study was procured from Global Nanotech, Mumbai (India). nHA (particle size up to 20 nm) was purchased from J.K. Impex, Mumbai (India). All other chemicals were procured from S.d.Fine Chem, Bangalore (India) and were used as received.

2.2. Silane treatment of nHA and NCF

10 g of nHA powder was mixed with 300 ml of dimethylformamide (DMF) and the mixture was stirred at reflux temperature (153 °C) under nitrogen atmosphere for 45 min. This was followed by drop wise addition of 5 ml of APTS. Then the reaction was allowed to occur in a locally fabricated microwave reactor (Enerzi Microwave Systems, India) for 1 h under reflux. After reaction, the modified nHA was separated by centrifugation (8000 rpm, 5 min) and washed with chloroform and absolute alcohol. The resulting modified nHA powder was dried in a vacuum oven at 60 °C for at least 24 h before use. Similar silane surface treatment was given to NCF to enhance dispersion and compatibility with the other components of the nanocomposites.

2.3. Blend preparation

Phosphate grafted PDMS (f-PDMS) was prepared by mixing MAEP and PDMS (10 ml of MAEP for 5 g of PDMS) in Brabender (Plasticorder, CMEI, 16CMESPL, East Germany) at 140 °C with rotor speed of 10 rpm for 5 min. The blend of PAEK/nHA/NCF and f-PDMS was prepared by melt mixing in Brabender (Plasticorder, CMEI, 16CMESPL, East Germany) at 372 °C with rotor speed of 20 rpm for 10 min by varying percentage of silane treated nHA (0%, 1%, 3%, 5%, 7%, 8% and 10%).

2.4. Compression molding

The blends obtained from Brabender plasticorder were pressed into sheets in a compression molding machine (Compression molding press, Santec, India) at 18 MPa pressure and 372 °C. The heating time was kept at 10 min and the curing time at 20 min.

2.5. Characterization

2.5.1. Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) spectra of nanocomposites were recorded between 600 and 4000 cm^{-1} using a Bruker ALPHA FT-IR Spectrometer. The samples were coated on a potassium bromide (KBr) plate and dried in a vacuum oven at 120 °C before it was tested.

2.5.2. X-ray diffraction (XRD)

X-ray diffraction measurements (XRD) for the composites were performed using advanced diffractometer [PAN alytical, XPERT-PRO] equipped with Cu-Kα radiation source ($X=0.154$ nm). The diffraction data were collected in the range of $2\theta=2$–60° using a fixed time mode with a step interval of 0.05°.

2.5.3. Scanning electron microscopy (SEM)

Scanning Electron Microscopy [SEM] (FEI QUANTA 200 microscope) was used to study the morphology of the fractured specimens. The specimens were gold sputtered prior to microcopy (JEOL, SM-1100E).

2.5.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) for nanocomposites was performed using a JEOL, Model 782, operating at 200 kV. TEM specimens were prepared by dispersing the composite powders in methanol by ultrasonication. A drop of the suspension was put on a TEM support grid (300 mesh copper grid coated with carbon). After drying in air, the composite powder remained attached to the grid and was viewed under the transmission electron microscope.