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Mechanical and structural characterization of diopside scaffolds reinforced with graphene

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ABSTRACT

Diopside (Di) is ideally suited for tissue engineering applications because of its good bioactivity and biocompatibility, while the low mechanical properties, such as strength and toughness, have hindered its application under load-bearing conditions. In this study, Di scaffolds fabricated by selective laser sintering (SLS) were reinforced with graphene nanoplatelets (GNPs). The mechanism of GNPs on mechanical properties of Di scaffolds was researched. The results showed that the compressive strength and fracture toughness of 1 wt % GNPs/Di scaffold were improved by 102% and 34%, respectively, compared with those of Di scaffold without GNPs. It may be ascribed to the uniform distribution of GNPs in the Di matrix and the grain refinement. Moreover, there exist crack bridging, crack deflection, crack branching and GNPs pullout mechanisms. Furthermore, continuous apatite layers were formed on the scaffolds in SBF solution and MG-63 cells presented good attachment and spreading on the scaffolds in vitro.

1. Introduction

Diopside (Di) in the $CaO-SiO_2-MgO$ system has been investigated as a potential candidate for bone repair and replacement owing to its perfect bioactivity and biocompatibility [1–3]. The release of Ca and Si ions can enhance gene expression and stimulate osteoblasts adhesion and spreading. Mg ion involves in many biochemical reactions and plays a significant important role [4,5]. In addition, Di can trigger the growth of apatite layers which have a similar composition with natural bone [6]. However, the insufficient strength and toughness of Di have been serious obstacles that limit its use in load-bearing parts. Appropriate strength and toughness are regarded as a vital requirement of bone scaffolds in process of new bone formation [7–9].

Graphene, an ultra-thin layer of carbon atoms arranged in a planar hexagonal lattice, has been heralded as a wonderful reinforcing component for composite materials due to its unique qualities, which include fascinating mechanical properties and specific geometric features [10–13]. Recent findings demonstrated the mechanical performance of polymer and ceramic based composites can be profoundly improved by additive of graphene. Pinto reported that plasticized poly (lactic acid) (PLA) nanocomposite films exhibited Young's modulus and yield strength about 100% higher than those of pristine PLA [14]. Ajayan prepared cement and concrete composites filled with hexagonal boron nitride and graphite oxide (GO), and the superior enhancement in mechanical properties by the incorporation of graphite oxide was illustrated [15]. Mehdi Mehrali et al. fabricated calcium silicate (CS) composites reinforced with graphene for tissue repair and replacement. The composites were prepared using hot isostatic pressing (HIP) and the fracture toughness, hardness and brittleness index were improved by 130%, 30% and 40% as compared to the CS without graphene [16]. Moreover, graphene was proved to be biocompatible with human fetal osteoblasts [17].

In general, a bioactive and biocompatible porous scaffold for

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tissue engineering acts as a temporary template for cell attachment, proliferation, differentiation and subsequent tissue generation [18–20]. SLS has more advantages over the conventional sintering methods such as HIP and spark plasma sintering (SPS) due to its ability of fabricating porous scaffolds.

In this study, the scaffolds prepared by SLS were reinforced with graphene nanoplatelets (GNPs) consisting of a few layers of graphene. The variation of the mechanical performance of the scaffolds with respect to the amount of GNPs has been systemically investigated. The microstructure and phase composition of the scaffolds were evaluated by SEM, X-ray diffraction (XRD) and Raman spectroscopy techniques. In addition, the bioactivity and biocompatibility of the scaffolds were evaluated by the apatite-forming ability and the adhesion and proliferation capacities of MG-63cells.

2. Materials and methods

2.1. Material preparation

The Di powder (particle size: ~200 nm) from Kunshan Chinese Technology New Materials Co., Ltd. (Kunshan, China) was employed as raw materials. GNPs were purchased from Nanjing XFNano Materials Tech Co., Ltd (Nanjing, China) and used as the reinforcement. Graphene was prepared by micromechanical exfoliation of graphite according to Geim and Novoselov [21]. The diameter of GNPs ranges between 0.5 and 2 μm, and sheet thickness is about 0.8 nm.

GNPs are prone to agglomerating for their strong π–π stacking between layers, posing a big obstacle for their applications in reinforcing ceramic matrix [22,23]. Therefore, the great challenge is to obtain uniform and homogeneous dispersions of GNPs in the ceramic matrix. In this study, appropriate amounts of GNPs and Di powder were added to separate containers of Dimethylformamide (DMF). The GNPs and Di solutions were sonicated using ultrasonic cleaning instrument (Kudos, SK3300H, 59 kHz) for 1 h, respectively. The dispersed solutions were then combined and sonicated for an additional 30 min before ball milling. Subsequently, the composite was dried in vacuum drying oven at 100 °C for 1 day. The chosen composites for this study were GNPs/Di composites with GNPs contents of 0.5, 1.0, 1.5, 2.0 wt %, respectively.

2.2. Fabrication and structural characterization

Di scaffolds with different contents of GNPs were prepared with a homemade SLS system (Fig. 1). In the SLS process, the composite powder was paved by a scraper onto the elevator. A laser beam selectively sintered the powder bed, and a solid layer was formed. Then the working platform was lowered by the thickness of a layer and a fresh powder layer was spread on the sintered part. The process was repeated until the three-dimensional scaffolds were completed. Scaffolds with different GNPs contents were marked as 0.5 wt % GNPs/Di, 1 wt % GNPs/Di, 1.5 wt % GNPs/Di, 2 wt % GNPs/Di, respectively.

The morphology of the raw powders and microstructures of the fabricated scaffolds were examined with scanning electron microscope MIRA 3 LMU (TESCAN, Czech Republic) at acceleration voltage of 20 KV. Before observation, the powders and the scaffolds were coated with gold (JEOL JFC-1600 Auto Fine Coater, Tokyo, Japan). Phase compositions of the scaffolds were identified by XRD (Bruker D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα radiation in the 2θ range from 20° to 60°. In order to confirm the structural integrity of GNPs within the Di after sintering, Raman analysis were recorded on a laser Raman spectrometer (Horiba Jobin Yvon LabRam HR800) with an excitation wavelength of 488 nm and at least 5 scans were done for each scaffold. Besides, scaffolds were polished and thermally etched at 1150 °C for 30 min in a muffle furnace for grain size study.

2.3. Mechanical properties assessment

The compressive strength was detected using a microcomputer control electronic testing machine (WD-D1, Shanghai Zhuoji instruments Co. Ltd, China) at a crosshead speed of 0.5 mm/min. Prior to the tests, the scaffolds were ground and then polished in order to obtain regular surfaces. Subsequently, ultrasonic cleaning was used to remove surface debris, followed by drying in hot air.

Fracture toughness (K_{IC}) was evaluated with a Digital Micro Hardness Tester (HXD-1000TM/LCD, Shanghai Taiming Optical Instrument Co. Ltd, China). Prior to indentation, all of the strut samples ($3 \times 1.6 \times 0.8$ mm^3) were vertically inlaid in epoxy with an inlaying machine (XQ-2B, Φ22*15). Then, the surface of the sample was polished using a grinding & polishing machine (Model MP-2, Laizhou Weiyi Experiment Machine Manufacturing Co., Ltd,

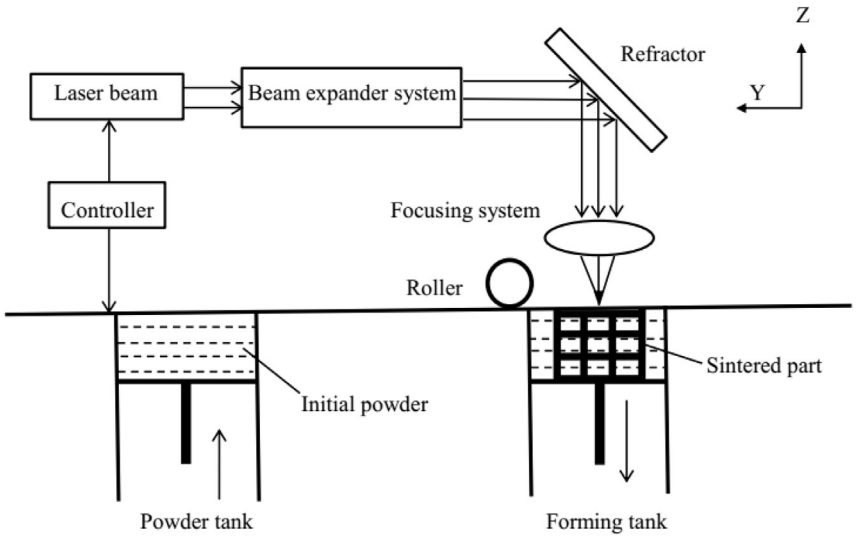

Fig. 1. Schematic drawing of the homemade SLS system.