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In vitro bioactivity and mechanical properties of bioactive glass nanoparticles/polycaprolactone composites

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ABSTRACT

Nanoparticles of bioactive glass (NBG) with a diameter of 50–90 nm were synthesized using the Stöber method. NBG/PCL composites with different NBG contents (0 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.%) were prepared by a melt blending and thermal injection moulding technique, and characterized with XRD, FTIR, and SEM to study the effect of NBG on the mechanical properties and in vitro bioactivity of the NBG/PCL composites. In spite of the high addition up to 40 wt.%, the NBG could be dispersed homogeneously in the PCL matrix. The elastic modulus of the NBG/PCL composites was improved remarkably from 198 ± 13 MPa to 851 ± 43 MPa, meanwhile the tensile strength was retained in the range of 19–21.5 MPa. The hydrophilic property and degradation behavior of the NBG/PCL composites were also improved with the addition of the NBG. Moreover, the composites with high NBG content showed outstanding in vitro bioactivity after being immersed in simulated body fluid, which could be attributed to the excellent bioactivity of the synthesized NBG.

1. Introduction

As an important part of tissue engineering research, bone tissue engineering, especially in the aspect of tissue repair and regeneration has attracted many researchers. Natural hard tissues are composite materials, consisting of organic matrixes such as collagen, together with glycoprotein and ceramics similar to nanocrystalline hydroxyapatite (HA) [1]. For hard tissue applications, biodegradable polymers, such as poly(L-lactic acid) [2–4], polycaprolactone (PCL) [5–7], poly(L-lactide/ε-caprolactone) copolymers [8], poly(lactide-co-glycolide) [9,10], poly(3-hydroxybutyrate) [11,12] and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [13], have been widely used because of their favorable biocompatibility and degradability. Among these polymers, PCL, a semi-crystalline linear aliphatic polyester with a high degree of crystallinity and hydrophobicity, approved by the Food and Drug Administration (FDA), has been extensively used for tissue regeneration owing to its cost-effectiveness, high toughness, excellent biocompatibility and biodegradability [1,14]. Moreover, the relatively high mechanical strength and low degradation rate of PCL provided PCL composites various advantages for application in bone tissue engineering with long term implantation period [15]. PCL nanofibers containing bioactive glass (BG) nanoparticles and simvastatin drug were prepared by electrospinning [16]. The in vitro bioactivity and drug release behavior of the PCL/BG nanofibers were studied.

From a material viewpoint, natural bones are composites composed of biopolymers and inorganic nanocrystals. There is about 69 wt.% HA in human bones. This fact implies that polymer based composites containing bioactive inorganic phases could be promising materials for bone regenerative matrixes as these materials could provide sufficient mechanical strength accompanied with excellent osteoconductivity and bioactivity [17–19]. It has been proved that addition of silica nanoparticles into poly(vinyl alcohol) can significantly improve the mechanical properties of the poly(vinyl alcohol) film [20]. Among the bioactive inorganic materials, bioactive glasses (BGs) have attracted much attention due to their excellent ability to chemically bond with living hard tissue through the formation of a bone mineral-like HA phase on the material surface that ultimately induces direct bonding with native bone tissue, which is their so-called bioactivity [1,21,22]. Many groups prepared macroporous structures for tissue engineering by mixing BG particles and biopolymers [23–27]. These BG particles were usually prepared by mechanically grinding bulk BGs synthesized by a melt-quenching or sol–gel process, thus had a wide range of particle size in micrometer scale. These big particles formed a dispersed phase in a biopolymer matrix and could lead to nonuniform surface bioactivity and mechanical properties [28]. In most cases, the content of BG particles was not more than 20 wt.% [11,17,29,30]. Enhancement of BG content could lead to an evident decrease in mechanical properties of BG/biopolymer composites due to the big defect caused by the interface separation between micrometer scale BG particles and biopolymer matrix. Cells cultured on a BG/biopolymer composite tended to nonuniformly attach and proliferate on the area where BGs gathered because particle aggregation could promote the roughness and wettability of the composite surface,

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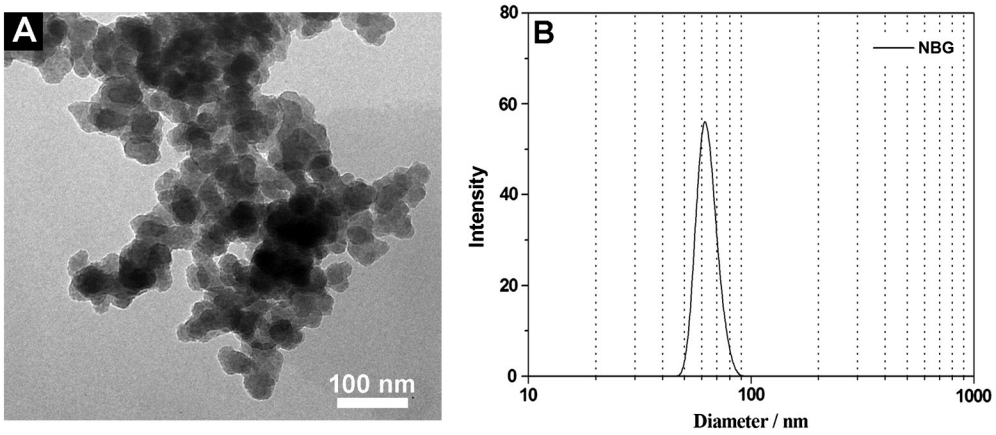

Fig. 1. A. A typical TEM image of NBG; B. the particle size distribution of NBG measured by DLS.

which had positive impacts on the adherence of cells [12,30,31]. However, considering that natural bones have a high content of HA crystals (about 69 wt.%), there is a great potential to improve the integrated properties of BG/biopolymer composites by enhancing its BG content. A possible solution is using nanoscale BG particles as tiny as HA crystals in natural bones. BG nanoparticles uniformly dispersed in a biopolymer matrix could be helpful for the formation of uniform properties [28]. The high surface area of nanoparticles could enhance the surface interaction between a BG and biopolymer matrix, and decrease the effect of phase separation.

Herein, the authors synthesized nanoparticles of bioactive glass (NBG) and investigated the effect of NBG content on the mechanical properties and in vitro bioactivity of PCL composites. The study aims at improving the bioactivity and mechanical properties of the NBG/PCL composite by enhancing the content of NBG in the PCL matrix.

2. Materials and method

2.1. Materials

Tetraethyl orthosilicate (TEOS), ethyl alcohol (EtOH), calcium nitrate tetrahydrate (CaNT), and ammonia hydroxide (28 wt.%), purchased from Sinopharm Chemical Reagent Co., Ltd., were all analytical grade and used directly without further purification. Poly(ε-caprolactone) (PCL, average Mn = 80,000) was purchased from Solvay (Shanghai) Co., Ltd. Deionized water was obtained from a Millipore water purification system.

2.2. Synthesis of NBG

NBG with a mole composition of 75% SiO_2 and 25% CaO (75S25C) were synthesized through the alkali-mediated Stöber method [32]. For a typical synthesis, water (10.95 g), EtOH (187.06 g), and ammonia hydroxide (2.88 g) were mixed together in a conical flask with magnetic stirring at room temperature for 15 min; and then CaNT (3.07 g) was added into the conical flask and dissolved under stirring. Additional amount of ammonia hydroxide was added to adjust the pH of the solution to be around 9.0. TEOS (8.08 g) was added into the previous solution and the solution was continuously stirred for 3 h. After standing the solution for about 6 h and removing the supernatant, NBG were obtained. The NBG were washed with ethanol several times and dried at 60 °C, and eventually calcined at 600 °C in air for 3 h with a heating rate of 5 °C/min.

2.3. Preparation of NBG/PCL composites

The NBG/PCL composites were produced through a melt blending and thermal injection moulding technique. The synthesized NBG and PCL were blended at 100 °C by a HAAKE Polydrive Mixer (Thermo Fisher Scientific, China) to prepare composites with different NBG contents (10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%). Finally, the NBG/PCL composites were processed into different shapes at 30–120 °C under a pressure of 700 MPa by a HAAKE MiniJet II (Thermo Fisher Scientific, China) and kept for further characterization.

2.4. Material characterization

A transmission electron microscope (TEM) (TECNAI-12, Philips, Holland) and a field emission scanning electron microscope (FE-SEM) (S-4800II, Japan) were used to characterize the surface morphology and microstructure of the NBG and NBG/PCL composites. The samples were sputtered with Au before SEM observation. The size distribution of the NBG was determined by dynamic light scattering (DLS) (Mastersizer 2000, Malvern, England). The chemical composition of the NBG and NBG/PCL composites was examined by Fourier transform infrared spectroscopy (FTIR, Tensor27, Bruke, Germany).

2.5. Mechanical properties

The NBG/PCL composites were prepared to be dumbbell shape samples of 75 × 12.5 × 2 mm (ISO 527-2-A5). Tensile strength, elastic modulus and elongation at break were measured by a universal mechanical testing machine (Instron 3367, USA) at a drawing speed of 50 mm/min at room temperature of 25 ± 1 °C and relative humidity of 60–65%. The average and standard deviation results of each composite were acquired by measuring five specimens.

2.6. In vitro bioactivity

The in vitro bioactivity of each composite was assessed by immerging samples in standard simulated body fluid (SBF) at 37 °C. The inorganic ion concentrations of SBF were 142.0 mM Na^+, 5 mM K^+, 1.5 mM Mg^{2+}, 2.5 mM Ca^{2+}, 147.8 mM Cl^-, 4.2 mM HCO_3^-, 1.0 mM

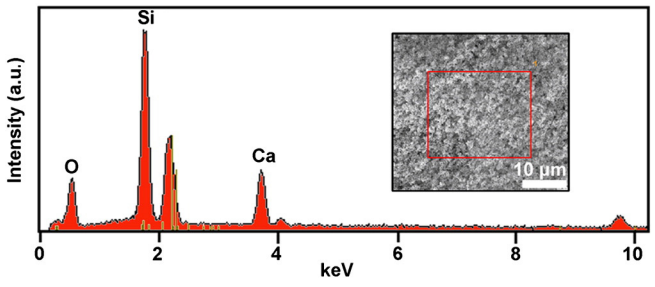

Fig. 2. Elemental distribution analysis of the synthesized NBG particles.