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Production and characterization of calcium phosphate (CaP) whisker-reinforced poly(ε-caprolactone) composites as bone regenerative

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ABSTRACT

Calcium phosphate (CaP) whisker-reinforced poly(ε-caprolactone) (PCL) composites with various CaP contents (0, 5, 10, and 20 wt.%) were prepared by dispersing CaP whiskers in a PCL solution. To accomplish this, CaP whiskers were synthesized by treating tricalcium phosphate (TCP) powders in a hydrogen peroxide (H_2O_2) solution at 90 °C for 48 h. All the prepared composites showed well dispersed CaP whiskers in the PCL matrix without severe agglomeration. As the CaP content was increased from 0 to 20 wt.%, the ultimate tensile strength decreased from 13.2 ± 0.9 to 8.8 ± 0.4 MPa, while the elastic modulus increased significantly from 173 ± 21 to 334 ± 24 MPa. In addition, the addition of CaP whiskers to the PCL matrix improved the biocompatibility of the composites remarkably.

1. Introduction

The reinforcement of biodegradable polymers with bioactive calcium phosphate (CaP) materials has attracted considerable attention for applications in bone tissue engineering because it can provide improved mechanical and biological properties compared to pure polymers [1–5]. Fundamentally, the mechanical and biological properties of CaP-reinforced polymer composites should be strongly affected not only by the content of the CaP particles in the composites [6], but also by the intrinsic characteristics of the CaP phase, including its chemical composition and shape [7].

Thus far, a variety of CaP particles with different shapes (e.g., spherical shape [8,9], needle-like nanocrystals [10], nanorods [11], and whiskers [6,12]) have been synthesized using a range of processing routes. However, relatively less attention has been paid to the possibility of using various CaP particles as reinforcements, even though they would be expected to allow composites to mimic the anisotropic mechanical and biological properties of natural bone [6,12].

Therefore, in this study, we examined the potential of CaP whiskers as a reinforcement of poly(ε-caprolactone) (PCL) polymer, which is one of the most-widely used biodegradable polymers with the proper strength and flexibility. To accomplish this, solvent casting that has been widely used to prepare polymer-based materials on account of its easy processability with high uniformity [13,14] was used to prepare the CaP whisker-reinforced PCL composites. The mechanical properties and biological behavior of the PCL/CaP composites with various contents of CaP whiskers (0, 5, 10, and 20 wt.%) were examined to evaluate their potential applications as bone regeneratives.

2. Experimental

The calcium phosphate (CaP) whiskers were synthesized by treating tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) with a hydrogen peroxide (H_2O_2) solution at 90 °C [12]. First, the as-received TCP (Alfa Aesar Co., Milwaukee, WI, USA) powders were calcined at 900 °C for 2 h to obtain well crystallized β-TCP powders. Thereafter, a 40 cc hydrogen peroxide suspension containing the 1.6 g TCP powders with a pH of 3.78 was placed in a drying oven at 90 °C for 48 h to allow the formation of CaP whiskers, followed by washing with distilled water and drying at 90 °C for more than 24 h.

Poly(ε-caprolactone) (PCL)/CaP whisker composites with a range of CaP contents (0, 5, 10, and 20 wt.%) were produced using the solution-casting method. More specifically, the predetermined amount of the synthesized CaP whiskers was added to dichloroethane (DCE, Sigma Aldrich, St. Louis, MO, USA), which was used as the solvent for the PCL polymer, and sonicated for 1 h to disperse CaP whiskers homogenously. Subsequently, the PCL pellets (Sigma Aldrich, St. Louis, MO, USA) was added to the CaP whiskers-containing DCE solvent and stirred mechanically for 2 h to achieve a homogenous solution. The prepared solution was then poured into a glass Petri dish, and dried at room temperature, resulting in the formation of the PCL/CaP whisker composites.

The microstructures and crystalline phases of the synthesized CaP whiskers and PCL/CaP composites were characterized by scanning electron microscopy (SEM, JSM-6360, JEOL Techniques, Tokyo, Japan) and X-ray diffraction(XRD, M18XHF-SRA, Mac science Co., Yokohama,

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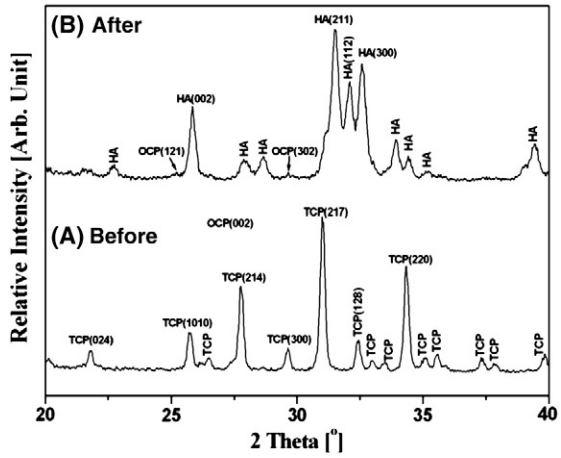

Fig. 1. Typical XRD patterns of (A) starting TCP powders and (B) synthesized CaP whiskers after treatment in a hydrogen peroxide solution at 90 °C for 48 h.

Japan), respectively. In addition, tensile strength tests were carried out to evaluate the mechanical properties of the PCL/CaP whisker composites. The samples were removed from the glass Petri dish and cut into a strip with dimensions of ~700 μm × 3 mm × 30 mm with scissors carefully. The samples were loaded at a crosshead speed of 0.2 mm/min using a screw driven load frame (Instron 5565, Instron Corp., Canton, MA, USA). The stress and strain responses of the samples during the tensile strength tests were monitored. Five samples were tested to obtain the mean and standard deviation.

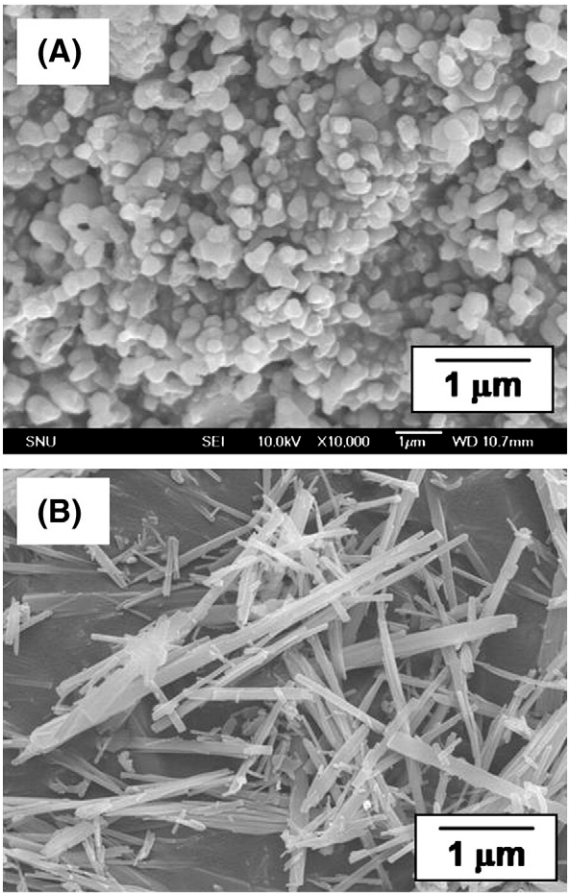

Fig. 2. Typical SEM micrographs of (A) the starting TCP powders and (B) the synthesized CaP whiskers after treatment in a hydrogen peroxide solution at 90 °C for 48 h.

In vitro cell tests of the PCL/CaP whisker composites were carried out using a pre-osteoblast cell line (MC3T3-E1; ATCC, CRL-2593, USA). For the initial cell attachment, proliferation and differentiation tests, the cells were plated at a density of 5×10^4 cells/ml and cultured in a humidified incubator in an atmosphere containing 5% CO_2 at 37 °C. Minimum essential medium (α-MEM: Welgene Co., Ltd., Seoul, Korea) supplemented with 10% FBS, 1% penicillin-streptomycin, 1, 3 and 10 mM β-GP, and 50 μg/ml ascorbic acid was used as the culturing medium. The cell attachment was observed by confocal laser scanning microscopy (CLSM, Zeiss-LSM510, Carl Zeiss Inc., NY, USA) after culturing for 15 h. The alkaline phosphatase (ALP) activity as an early marker of the maintenance of the osteoblastic phenotype using p-nitrophenyl phosphate (pNPP) (Sigma-Aldrich, UK), was measured after culturing for 14 days [15]. All experiments were performed

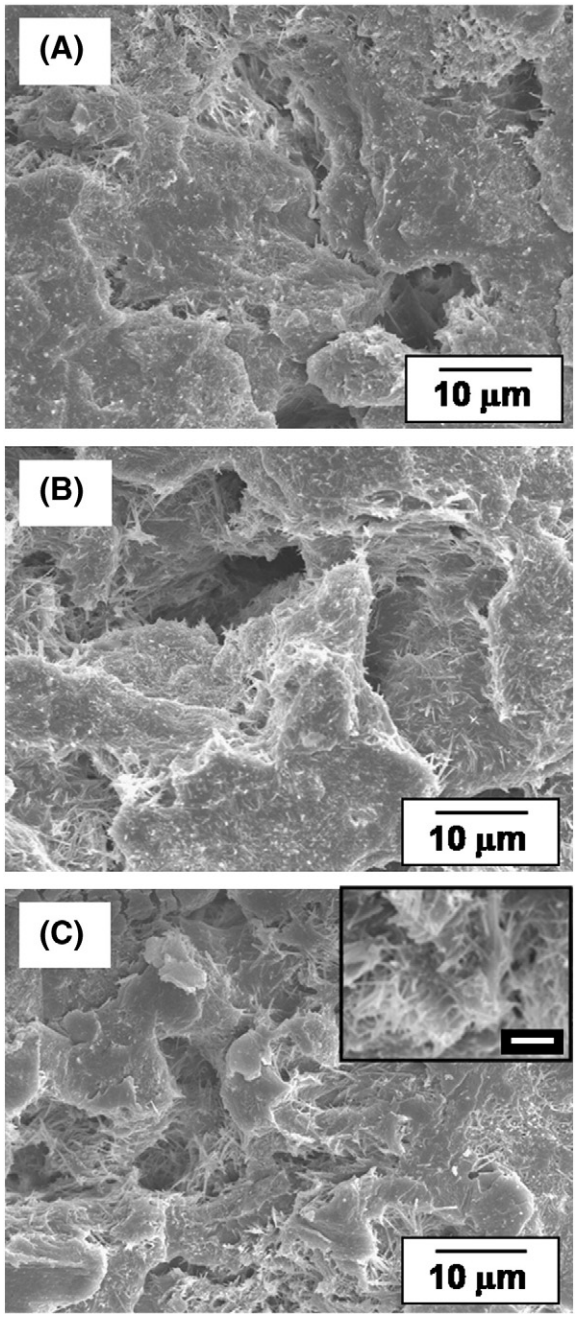

Fig. 3. Typical SEM micrographs of the PCL/CaP composites with various CaP contents of (A) 5, (B) 10, and (C) 20 wt.%. The inset in Fig. 3(C) shows the typical SEM micrograph of the composite at a higher magnification.