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Electrospun Calcium Metaphosphate Nanofibers: I. Fabrication

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ABSTRACT

Calcium metaphosphate (CMP) nanofibers with a diameter of ~600 nm were prepared using electrospun CMP/polyvinylpyrrolidone (PVP) fibers through a process of drying for 5 h in air followed by annealing for 1 h at 650°C in a vacuum. The viscosity of the CMP/PVP precursor containing 0.15 g/ml of PVP was 76 cP. Thermal analysis results revealed that the fibers were crystallized at 569°C. The crystal phase of the as-annealed fiber was determined to be δ-CMP (δ-$Ca(PO_3)_2$). However, the morphology of the fibers changed from smooth and uniform (as-spun fibers) to linked-particle characteristics with a tubular form, most likely due to the decomposition of the inner PVP matrix. It is expected that this large amount of available surface area has the potential to provide unusually high bioactivity and fast responses in clinical hard tissue applications.

Key words **: *Calcium metaphosphate, Nanofiber, Electrospinning, Polyvinylpyrrolidone***

1. Introduction

The increased demand for restorative treatment in dentistry and orthopedics has fueled the development and introduction of synthetic bioactive glasses for clinical hard tissue applications.[1-6] Over the last decade, bioactive glasses have been widely researched as the associated apatite formation promotes the bone formation and induces bonding to the living tissue. The apatite layer is formed when the glasses are soaked in a physiological solution. It has been reported that the surface activity of the bioactive glasses is responsible for the high rates of bone regeneration.[5]

Although apatite has excellent bioactivity characteristics, the interface disruption between apatite and an implant limits its long-term clinical use.[4] It is also known that hydroxyapatite and tricalcium phosphate are characterized by low toughness, low elasticity, a low resorbtion qualities, and lack of osteogenic properties.[7] Bioresorbable glass ceramics containing biodegradable calcium metaphosphate (CMP, $[Ca(PO_3)_2]_n$) have been considered as the candidate material of choice for bone-graft applications due to their biodegradability and osteconductivity.[4,6] From a study of the retrieved CMP scaffold from rat femoral transplants, it was reported that non-fibrous tissues at the interface between the host tissue and the scaffold material demonstrated that CMP possesses excellent biocompatibility and biodegradability characteristics.[8]

Due to their unique properties, one-dimensional nanostructures are useful in a wealth of applications, including electronics, optoelectronics, mechanics, catalysis, and biological and environmental systems.[9-12] Among various synthetic methods, electrospinning (ES) is employed to synthesize fibular mesostructures for simplicity.[13-17] ES is a method of producing nanoscale fibers for application to bone-tissue regeneration by accelerating a jet of charged solution in an electric field. CMP sol with a Ca/P ratio of 0.5, the subject of this study, was prepared by the conventional sol-gel process.[4] Prior to ES, polyvinylpyrrolidone (PVP) dissolved in ethanol was added to the CMP sol to control the solution viscosity. The CMP fibers were examined by scanning electron microscopy (SEM), thermal gravimetry with differential scanning calorimetry (TG/DSC), and X-ray diffraction (XRD) to investigate the morphology and microstructure of the resulting fibers.

2. Experimental Procedure

A precursor solution was prepared from calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, 99%, Aldrich, USA) and triethyl phosphite ($(C_2H_5O)_3P$, 98%, Aldrich, USA) in methanol (99.8%, Junsei, Japan) by stirring. The sol-gel process was conducted in an Ar atmosphere, as shown in Fig. 1. The detailed experimental procedure is described elsewhere.[4] Gelation of the sol was achieved by drying in an oven for 6 h at 150°C. The powders were then heat-treated for 1 h at 650°C in a vacuum with a heating rate of 2°C/min up to 150°C, 1°C/min at temperatures ranging from 170 to 300°C, and 3°C/min at temperatures between 300 and 650°C.[4] The stoichiometry of the powders was evaluated with thermal gravimetry with differential scanning calorimetry (TG/DSC,

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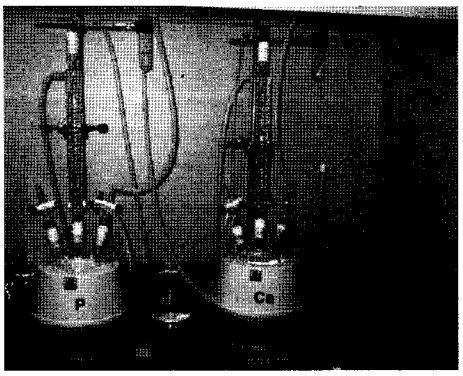

Fig. 1. Experimental apparatus for CMP sol.

Netzsch STA 409C/31F, Germany) and X-ray diffraction (XRD, Mac Science, KFX-987228-SE, Japan).[13] TG/DSC was performed in the temperature range of room temperature to 1000°C with a heating rate of 10°C/min. XRD was carried out with a scan speed of 5° 2θ/min in the 2θ range of 20 to 80°.

Prior to ES, polyvinylpyrrolidone (PVP, Mw= 1,300,000, Aldrich, USA) dissolved in ethanol was added to the CMP precursor solution by weight according to the rheological properties of the sol.[3,4] It is known that PVP has good solubility in alcohols and water.[3-5] The resistivity rose as alcohol was added, as alcohol has a resistivity that is at least two orders of magnitude greater than that of water.

The ES apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22-gage B-D metal needle, a grounded collector and a high-voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters.[13,15,17] The solution was placed in a 5-ml B-D Luer-lok syringe attached to the syringe pump and was fed into the metal needle at a flow rate of 0.5 mL/h. A piece of flat aluminum foil was placed 10 cm below the tip of the needle to collect nanofibers at a DC voltage of 10 kV. Flat mats that could be either fabricated or cut to almost any size represent an attractive form for use with typical tissue applications. The as-spun nanofibers were dried for 5 h in air.

The kinematic viscosity was measured with a 200-gage Cannon-Fenske viscometer, while the density was measured by pycnometer. The dynamic viscosity was calculated from the kinematic viscosity and density data.[16,17] The diameter and the morphology of the fibers were evaluated using a scanning electron microscope (SEM, Hitachi S-3000H, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. For SEM observation, CMP fibers were collected by placing silicon wafers on aluminum foil during electrospinning.

3. Results and Discussion

The thermal decomposition behavior of the CMP gel dried for 6 h at 150°C was investigated to determine the crystallization (T_c) and melting temperatures (T_m). The endothermic peak at 244°C in the DSC curve was observed due to the

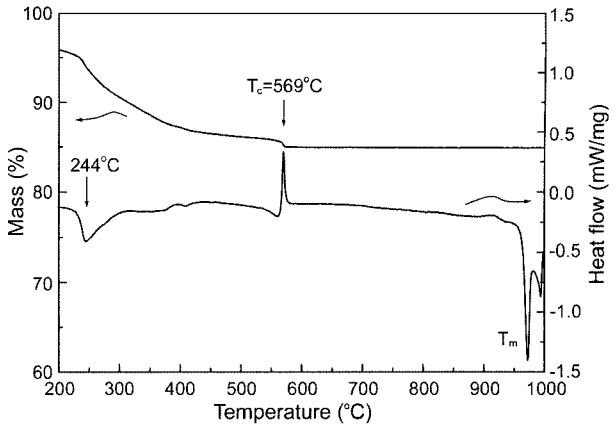

Fig. 2. TG/DSC curves of the calcium metaphosphate gel.

evaporation of the solvent. The mass loss was nearly 7% of the initial weight, as can be seen in Fig. 2. Another mass loss appeared at temperatures between 562°C and 573°C. The mass loss at this stage is ascribed to the formation of δ-CMP by the elimination of nitrates introduced as calcium nitrate in the preparation of the sol.[18] The exothermic peak at 569°C (T_c) corresponds to the crystallization of δ-CMP. Two endothermic peaks at temperatures (T_m) of 972°C and 993°C indicate the melting caused by the partial melting of the crystalline phases or residual glass matrix.[7] Therefore, it is conceivable that the annealing temperature should be higher than 569°C to obtain δ-CMP. XRD results (Fig. 3) revealed that the crystalline phase of the glass after a heat treatment for 1 h at 650°C in a vacuum was determined to be δ-CMP (δ-$Ca(PO_3)_2$, JCPDS-9-363),[4,6,19] which was confirmed by the TG/DSC results.

The viscosity of the CMP sol was adjusted by adding PVP. The variation of the viscosity of the precursor solution as a function of the PVP concentration is presented in Fig. 4. The viscosity of the CMP sol was 2.5 cP, which is inadequate for ES. In addition, no fibers were observed in a CMP solution containing less than 0.10 g/ml of PVP, most likely due to the low viscosity. The viscosity (fiber diameter) increased grad-

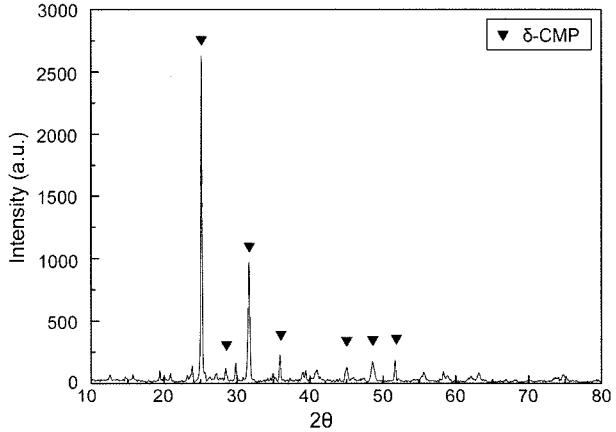

Fig. 3. XRD pattern of the CMP gels heat-treated for 1 h at 650°C in vacuum.

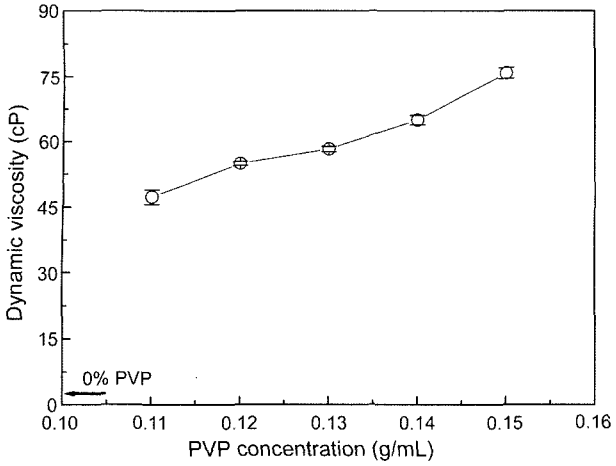

Fig. 4. The variation of solution viscosity as a function of the PVP concentration. The flow rate and electric field were 0.5 ml/h and 1 kV/cm.

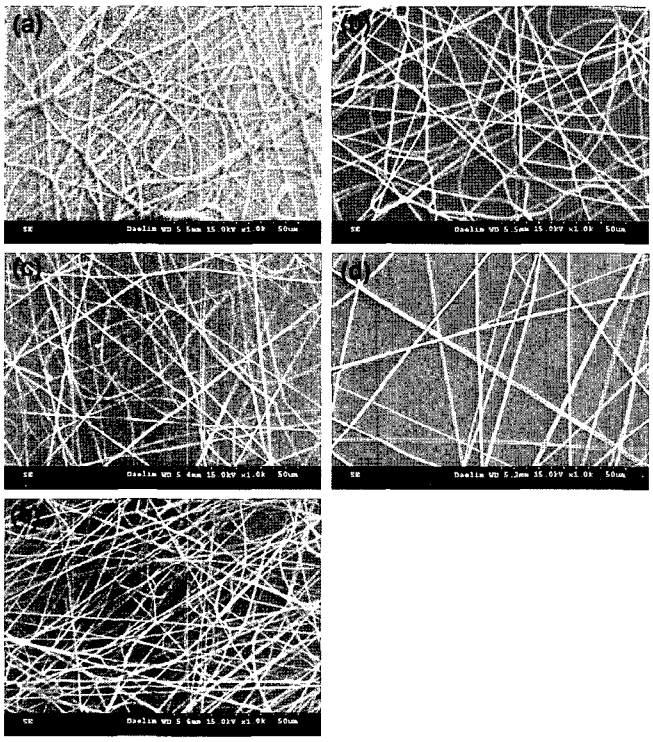

Fig. 5. SEM micrographs of electrospun CMP fibers containing various PVP concentrations: (a) 0.11 g/ml; (b) 0.12 g/ml; (c) 0.13 g/ml; (d) 0.14 g/ml; and (e) 0.15 g/ml, respectively. The flow rate and electric field were 0.5 ml/h and 1 kV/cm.

ually from 47 to 76 cP as the PVP concentration increased from 0.11 to 0.15 g/ml, as depicted in Figs. 4 and 5. It was reported that metal oxide (TiO_2) fibers having a viscosity lower than ~60 cP become discontinuous during annealing at 500°C.[13] The CMP sol containing 0.15 g/ml of PVP was selected in the present work to prevent fiber breakage during annealing, as the CMP became crystallized at 650°C.

The morphology of the as-spun and as-annealed fibers was

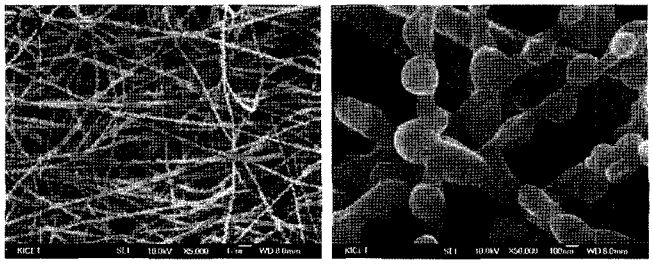

Fig. 6. (a) Low and (b) high magnification SEM images of fibers containing a PVP concentration of 0.15 g/ml. The fibers were annealed for 1 h at 650°C in a vacuum.

examined by SEM, as shown in Figs. 5 and 6. The images of the as-spun fibers (Fig. 5) show that the nanofibers have smooth and uniform surfaces with random orientation.[16] However, the as-annealed fibers have changed and appear to consist of linked particles or crystallites. This is in all probability due to the formation of the particulate morphology. Fig. 6 demonstrates that the annealed fibers exist in tubular form due to the decomposition of the inner PVP matrix.[18]

CMP nanofibers with a diameter of ~600 nm were prepared successfully by ES. After annealing for 1 h at 650°C in a vacuum, the crystalline phase of the fiber was determined to be δ-CMP (δ-$Ca(PO_3)_2$). However, the morphology of the fibers changed from smooth and uniform to a linked-particle tubular form due to the decomposition of the inner PVP matrix. It is expected that this large amount of available surface area has the potential to provide unusually high bioactivity and fast response in clinical hard tissue applications.

4. Conclusions

Calcium metaphosphate (CMP) nanofibers with a diameter of ~600 nm were prepared using electrospun CMP/polyvinylpyrrolidone (PVP) fibers through a process of drying for 5 h in air followed by annealing for 1 h at 650°C in a vacuum. The viscosity of the CMP/PVP precursor containing 0.15 g/ml of PVP was 76 cP. TG/DTA results revealed that the fibers were crystallized completely to δ-CMP (δ-$Ca(PO_3)_2$) at 569°C. However, the morphology of the fibers was changed from smooth and uniform (as-spun fibers) to a linked-particle tubular form, which most likely resulted from the decomposition of the inner PVP matrix.

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