Improvement of compressive strength of porous hydroxyapatite scaffolds by adding polystyrene to camphene-based slurries

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**Abstract**

The compressive strength of porous hydroxyapatite (HA) scaffolds was enhanced by adding polystyrene (PS) polymer as a binder to hydroxyapatite (HA)/camphene slurries. As the PS content was increased from 0 to 20 vol.% in relation to the HA content, the compressive strength was significantly increased from 1.1±0.2 to 2.3±0.5 MPa, while the pore size was decreased from 277±47 to 170±29 µm. The improvement in the compressive strength was mainly attributed to both the suppression of the cracking of the green sample during freeze drying and the mitigation of the formation of micro-pores in the HA walls.

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**Introduction**

The freeze casting of a ceramic slurry has recently attracted increasing interest for the production of porous ceramics, in which interconnected pores are readily produced by removing the dendrites composed of the freezing vehicle (e.g., water [1,2], camphene [3,4], tert-butyl alcohol [5], water-dioxane mixture [6]) grown during solidification. More recently, we demonstrated that porous hydroxyapatite (HA) scaffolds with large interconnected pores with a size of >100 µm, which are favorable for bone ingrowth, could be obtained by freezing ceramic/camphene slurries near their solidification temperature, i.e., 35 °C [7,8]. However, when a low ceramic content is employed to increase the porosity, cracks are prone to occur in the green sample, because of shrinkage during freeze drying, which, consequently, causes a severe reduction in strength.

Therefore, in this study, we employed polystyrene (PS) polymer as the binder, since it would be expected to improve the strength of the green body, which, in turn, would prevent it from cracking [9]. To accomplish this, various PS contents (0, 10, 20, and 30 vol.% in relation to the HA content) were added to the HA/camphene slurries. The prepared slurries were frozen at 34 °C for 48 h and then freeze-dried, followed by sintering at 1250 °C for 3 h. The effect of the addition of PS on the development of the porous structure (i.e., pore size, pore shape, and densification of HA walls) and the compressive strength of the porous HA scaffolds was evaluated.

**2. Experimental procedure**

Commercially available hydroxyapatite (HA) powder (Ca10(PO4)6(OH)2; Alfa Aesar Co., Milwaukee, WI, USA) and camphene (C10H16; Alfa Aesar/Avocado Organics, Ward Hill, MA, USA) were used as the bioactive material and freezing vehicle, respectively. In addition, polystyrene (PS; [-CH2CH(CH3)]n; Mw=230,000 g mol⁻¹, Sigma Aldrich, St. Louis, MO, USA) was used as the binder. Firstly, HA powder calcined at 900 °C for 1 h was ball-milled with the molten camphene containing various PS contents (0, 10, 20, and 30 vol.% in relation to the HA content) with the aid of 6 wt.% of oligomeric polyester dispersant (Hypermer KD-4, UniQema, Everburg, Belgium) at 60 °C for 24 h. The initial HA content in the slurry was 10 vol.% The compositions of the HA/PS/camphene slurries used in this study are summarized in Table 1.

The prepared warm slurries were then poured into polystyrene (PE) molds with a diameter of 12.5 mm and kept at 34 °C for 48 h in a drying oven. After demolding, the green bodies were freeze dried for 24 h. Thereafter, the samples were heated from 200 to 600 °C in a slow heating rate of 1 °C/min and maintained at this temperature for 3 h to completely remove the PS binder without causing severe defects [9], followed by sintering at 1250 °C for 3 h to densify the HA walls. The fabricated samples were characterized by evaluating their pore structures (e.g., porosity, pore size, and densification of the HA walls) using scanning electron microscopy (SEM, JSM-6330F, JEOL Techniques, Tokyo, Japan). The porosity was calculated by measuring their dimensions and weight. The pore size was also analyzed from the SEM images of the samples prepared by infiltrating the porous HA scaffolds with an epoxy resin (Spurrs epoxy, Polysciences Inc., Warrington, PA).
In addition, the pore size distributions of the samples were also measured by mercury porosimetry (AutoPore IV 9500, Micromeritics Instrument Co., Norcross, GA, USA). The compressive strength of the porous HA scaffolds with a diameter of \( \sim 10 \) mm and a height of \( \sim 12 \) mm were measured using a screw driven load frame (Instron 5565, Instron Corp., Canton, MA, USA) at a crosshead speed of 5 mm/min. More than seven samples were tested to obtain the average value along with its standard deviation.

3. Results and discussion

Regardless of the PS content employed in the HA/camphene slurries, all of the prepared samples showed highly porous structures and excellent shape tolerance after sintering at 1250 °C for 3 h, as shown in Fig. 1(A)–(D). They also had similar porosities in the range of 71–73% (i.e. 71, 72, 73, and 73 for the samples produced using the PS contents of 0, 10, 20, and 30 vol.%, respectively). However, it was observed that the pore structure, such as the pore size and microstructure of the HA walls, was notably affected by the initial PS content.

The pore size was measured by considering the SEM images of the epoxy-filled samples. As the PS content was increased from 0 to 30 vol.%, the pore size was decreased from 277 ±47 to 141 ±11 \( \mu \)m, as shown in Fig. 2. However, it should be noted that the smallest pore size achieved in the sample prepared with a PS content of 30 vol.% is larger than 100 \( \mu \)m, which would allow the porous HA scaffolds prepared in this study to find very useful applications in bone tissue engineering.

So far, the overgrowth of camphene dendrites during freezing at a temperature close to the solidification point of the ceramic/camphene slurry is not well understood. However, it is obvious that the camphene dendrites can continue to overgrow when the slurry is kept at such a temperature (e.g. 34 °C), which is presumably related to their partial remelting [7,8]. Therefore, it is reasonable to suppose that the presence of the PS polymer employed in the slurry lowers its degree of supercooling [10,11], which will, consequently, slow down the continual overgrowth rate of the camphene dendrites, resulting in the formation of narrower pores in the sample.

The microstructure of the HA walls was significantly influenced by the PS content, as shown in Fig. 3(A)–(D). Without the addition of the PS polymer, a large number of micro-pores were formed both on and inside the HA walls (Fig. 3(A)). These micro-pores are believed to be generated as the replica of the protrusions between the secondary branches of the camphene dendrites [12]. In addition, some cracks caused by shrinkage during freeze drying were observed, as indicated by the arrows. When a PS content of 10 vol.% was employed, the sample still showed micro-pores inside the HA walls (Fig. 3(B)). However, their formation on the surface of the HA walls was notably suppressed (inset in Fig. 3(B)). These micro-pores inside the HA walls eventually disappeared, when a higher PS content of 20 vol.% was employed (Fig. 3(C)). As a consequence, the sample with 20 vol.% PS showed good densification of the HA walls without any noticeable micro-pores or cracks, while a number of irregular pores were formed on

### Table 1

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<th>Composition of HA/PS/camphene slurries used in this study</th>
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<td>PS: HA [vol.%]</td>
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*Theoretical density (g/cc): camphene (0.83 at 60 °C), HA (3.14), PS (1.05), KD4 (0.9).
the surface of the HA wall (inset in Fig. 3(C)), which were formed by the removal of the PS polymer, which is frequently used as the pore-forming agent [13,14]. It is believed that the PS phase first solidifies from the molten camphene by means of a thermally induced phase separation (TIPS) process during freezing and then traps the HA particles, which would result in a homogeneous mixture of HA/PS phase without any severe segregation, consequently, mitigating the extensive formation of micro-pores inside the HA walls. Using a higher PS content of 30 vol.% was found to hinder the densification of the HA walls, since the excessive PS binder would result in the formation of lots of small pores (Fig. 3(D)).

The generations of micro-pores in the HA walls were further examined using mercury porosimetry, as shown in Fig. 4(A)–(D). All of the fabricated samples showed similar patterns, in which lots of micro-pores with a size of several microns were formed on and/or inside the HA walls. However, it should be noted that relatively large pores with a size > 10 µm were also observed in the samples prepared using the PS polymer (Fig. 4(B)–(D)), which were presumably due to the removal of the PS polymer.

The compressive strength of the porous HA scaffolds was also significantly affected by the PS content, as shown in Fig. 5. As the PS content was increased from 0 to 20 vol.%, the compressive strength of the sample was significantly increased from 1.1±0.2 MPa to 2.3±0.5 MPa. This improvement was primarily attributed to both the suppression of the cracking of the green sample during freeze drying and the mitigation of the formation of micro-pores in the HA walls. However, a higher PS content of 30 vol.% was observed to lead to a lower compressive strength of 1.6±0.5 MPa, due to the presence of small pores formed by the removal of the PS polymer both on and inside the HA walls.

4. Conclusions

We herein demonstrated that the compressive strength of porous HA scaffolds could be significantly improved by simply adding PS polymer as a binder to the HA/camphene slurries. The PS binder was found to effectively prevent not only the cracking of the sample by increasing its green strength, but also the formation of micro-pores inside the sintered HA walls. The sample produced with a PS content

![Fig. 3. SEM micrographs of the porous HA scaffolds produced with initial PS contents of (A) 0 vol.%, (B) 10 vol.%, (C) 20 vol.%, and (D) 30 vol.%, showing the microstructures of the HA walls. The insets show the surface microstructures of the HA walls (scale=2 µm).](image)

![Fig. 4. Pore size distributions for the porous HA scaffolds produced with initial PS contents of (A) 0 vol.%, (B) 10 vol.%, (C) 20 vol.%, and (D) 30 vol.%.](image)

![Fig. 5. Compressive strengths of the porous HA scaffolds as a function of the PS content.](image)
of 20 vol.% showed the highest compressive strength of 2.3±0.5 MPa with a pore size of 170±29 µm, which means that it would find very useful applications in bone tissue engineering.

Acknowledgment

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References