Degradation Behavior of Porous Calcium Phosphates

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Abstract

Concerning an ideal scaffold, evaluation of many factors, such as porosity, porous size and mechanical properties are needed so as to investigate degradation behavior in addition to chemistry and structure of materials used. In this study, the porous calcium phosphates were made on addition of a pore-former compound (PVA) by sinter processing. Mechanical properties, morphology, and weight change in in vitro testing were assessed. Experimental results indicated macropore sizes as large as hundreds of micrometers were generated and many micropores were also observed in the sintered body. After immersion in Hanks’ solution, on the body surface there was a pitting appearance with immersion-induced micropores. The compressive strength of as-sintered bodies decreased steadily with addition of PVA. With increasing immersion time, the compressive strength and modulus of various porous bodies decreased and the weight loss increased. The biomedical uses of the present porous materials might limit to use as bone defect repair.

Keywords: Tissue engineering, Porous scaffold, Mechanical property, Calcium phosphate

Introduction

Tissue engineering is regarded as one of the bioscience for guiding body to regenerate or repair tissues, when organ and tissue lose or failure occurs [1-3]. The scaffold is a temporary supporting structure of tissue-engineered constructions and it needs to be selected carefully. The scaffold materials must be biocompatible and biodegradable with controllable degradation rates to match tissue replacement [1-2,4-5]. Besides suitable surface chemistry, the scaffold architecture provides sufficient space and suitable mechanical properties for the tissues regeneration [1-2]. Hence, the use of biodegradable biomaterials as bone scaffolds has attracted a great deal of attention and a variety of fabrication methods have been proposed to produce porous scaffolds with interconnected pore networks [3-6]. Porous biodegradable synthetic materials, such as calcium phosphates, poly(lactic acid) (PLA), and poly(glycolic acid) (PGA), are currently tested as implants for the regeneration of damaged and diseased tissues [2-4,7].

The available synthetic biodegradable calcium phosphate ceramics for bone tissue regeneration include hydroxyapatite (HA), β-tricalcium phosphate (β-TCP), and calcium polyphosphate [3,4,6,7]. The biodegradation behavior of calcium polyphosphate materials in both in vitro and in vivo has been reported [6-10]. Utilizing solid freeform fabrication to build porous parts of calcium polyphosphate, Porter et al. [8] found a decline in mechanical strength in tris-buffered solution. Lee et al. [9] suggested that the composite graft of marrow-derived mesenchymal cells and porous calcium polyphosphate may be useful for the repair of bone defects.

Few studies on the variations in mechanical properties of porous calcium phosphates, when immersed in simulated body fluid have been exploited. In the present study, porous calcium phosphates were prepared by sintering mixtures of monocalcium phosphate monohydrate (MCPM, Ca(H2PO4)2·H2O) and polyvinyl alcohol (PVA). To impart porosity to the ceramic body, the PVA was burned out during firing, leaving free space in the resulting body. The degradation behavior of porous bodies was characterized by monitoring changes in compressive strength, compressive modulus as well as weight loss in simulated physiological solution.

Materials and Methods

Commercially pure MCPM and PVA powders (Showa, Tokyo, Japan) were used. The as-received MCPM powder was directly mixed with PVA in a vacuum mixer (VM-112T, J.Morita, Saitama, Japan) for 5 minutes to ensure homogeneity. The biodegradation behavior of calcium polyphosphate materials in both in vitro and in vivo has been reported [6-10]. Utilizing solid freeform fabrication to build porous parts of calcium polyphosphate, Porter et al. [8] found a decline in mechanical strength in tris-buffered solution.* Corresponding author: Shinn-Jyh Ding
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Table 1. Chemical composition of Hanks’ physiological solution.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>8.00</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.35</td>
</tr>
<tr>
<td>KCl</td>
<td>0.40</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.14</td>
</tr>
<tr>
<td>Na₂HPO₄·2H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.06</td>
</tr>
<tr>
<td>Glucose</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Results and discussion

Morphology

The morphologies of a series of as-sintered porous bodies are shown in Fig. 1. The SEM micrographs showed the pore structure of calcium phosphate bodies can essentially be considered as an assembly of the macropores and micropores. Macropore sizes as large as hundreds of micrometers were generated and many micropores (< 10 µm) were also observed in the sintered body. It is obvious that introduction of PVA in the ceramic powder resulted in sintered bodies with macropores and micropores as desired.

When immersed in Hanks’ solution, although having a similar morphology, SEM observation revealed the signs of
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Figure 2. SEM micrographs of porous bodies prepared with the weight fractions of PVA particulates of (a) 25%, (b) 33%, (c) 40%, and (d) 50% after 90-day immersion in Hanks’ solution. Arrows indicate immersion-induced micropores.

degradation at all four samples possible due to the solution attack. The samples immersed for 90 days have a pitting appearance with large amounts of immersion-induced micropores of about several micrometers, as indicated by arrows in Fig. 2.

Weight loss

To further study the dissolution/degradation process, a series of weight change were performed for all immersed samples. Fig. 3 shows that all samples continue dissolving after immersion in Hanks’ solution. The dissolution behavior of immersed calcium phosphate materials in simulated physiological solution has been reported [10-12]. The result indicated that sample 50C50V had the fastest weight loss with degradation time. However, the weight loss remained about 6% over 90 days of immersion for all other samples. The loss in sample weight might be explained by degradation of such materials.

Compressive strength

The compressive strength of as-sintered calcium phosphates decreased steadily with addition of PVA, as listed in Table 2. The average compressive strengths and standard derivations of as-sintered 75C25V, 67C33V, 60C40V, and 50C50V bodies were 1.43 ± 0.09, 0.68 ± 0.07, 0.44 ± 0.05, and 0.10 ± 0.01 MPa, respectively. One-way ANOVA analysis showed that there is significant (p < 0.05). The samples with lower PVA contents had a higher compressive strength probably due to their less porosity. The decrease in the
The compressive strength with increased porosity was not surprising and has been described elsewhere [6,13]. LeHuec et al. suggested that total porosity and pore size influenced mechanical strength [13], which both related to the decrease in the quantity of solid material existed in each specimen.

The variations in the compressive strength with immersion time of the series of porous bodies are presented in Fig. 4. Six immersion regimes of 1, 3, 7, 15, 30, and 90 days were selected for testing the porous bodies. The mechanical properties of 90-day-immersed 50C50V are not available due to the lack of structural integrity and fracture during handling. It is evident that the compressive strength at any immersion time was subjected to a large standard deviation, probably because of the porosity characteristics. The results revealed that, when immersed in Hanks’ solution, the four different types of porous samples gradually lost their strength with increasing immersion time. For example, the initial strength of 0.68 MPa of sample 67C33V was significantly reduced down to 0.53 MPa after one-day immersion ($p < 0.05$). When immersed for 15, 30, and 90 days, its strength decreased to 0.29, 0.21, and 0.23 MPa, respectively. The statistical analysis using Scheffe multiple comparison testing showed that the compressive strength of immersed calcium phosphates mixed with 25 wt% PVA in green compact (75C25V) significantly declined by about 70% after immersion for 90 days ($p < 0.05$). When the green compacts comprised 33 and 40 wt% PVA, the resulting porous bodies lost 66% and 73% of their compressive strengths after 90-day immersion, respectively. This deterioration in the strength seems unavoidable for biodegradable porous ceramics immersed in simulated body fluid and has also been observed in other studies [6,8].

According to Porter et al., the immersion-induced decline in mechanical strength was due to less stable zones (particle surfaces or interface regions of grains) of porous ceramic body, where the degradation occurred more rapidly [8]. Besides the resulting porous structures of calcium phosphates as described above, the dissolution of the calcium phosphate in the solution and the penetration of water/ions resulting from the solution possibly accounted for the deterioration in mechanical properties [10-11].

### Table 2. Mechanical properties of as-sintered porous bodies.

<table>
<thead>
<tr>
<th>Code</th>
<th>Compressive strength ± SD (MPa)</th>
<th>Modulus ± SD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75C25V</td>
<td>1.43 ± 0.09</td>
<td>15.02 ± 1.18</td>
</tr>
<tr>
<td>67C33V</td>
<td>0.68 ± 0.07</td>
<td>12.51 ± 0.66</td>
</tr>
<tr>
<td>60C40V</td>
<td>0.44 ± 0.05</td>
<td>9.22 ± 0.44</td>
</tr>
<tr>
<td>50C50V</td>
<td>0.10 ± 0.01</td>
<td>0.96 ± 0.04</td>
</tr>
</tbody>
</table>

Modulus

The initial moduli of porous bodies also varied with the amounts of PVA (Table 2). The Young’s modulus decreased with increasing PVA content from 15.02 MPa for sample 75C25V to 0.96 MPa for sample 50C50V. As mentioned above, the samples with lower PVA contents had a less porosity and may be responsible for the greater modulus. The variations of compressive modulus against immersion time for porous bodies are shown in Fig. 5. After immersion in Hanks’ solution, there was a pronounced decrease in the modulus for all porous bodies but 50C50V body, similar trends with changes in compressive strength.
Conclusion

In this investigation, the obtained results showed the sample with lower PVA addition had a greater initial mechanical property. Hanks’ solution treatment imposed in our study did have a statistically significant effect on the compressive strength. The strength and modulus values of all immersed bodies largely declined. Due to their low strength and susceptibility to solution attack, the biomedical uses of the present porous materials might limit to use as bone defect repair.

References

多孔鈣磷酸鹽降解行為研究

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摘 要

理想的骨架除了考量材料本身的化性與結構外，需要評估其孔隙率、孔洞大小及機械性質等因素以研究降解性行為。本實驗添加孔原形成劑(PVA)，以燒結法製作多孔鈣磷酸骨架，將此種材料浸泡於 Hanks 模擬體液中，研究其機械強度變化及重量損失，並觀察微結構形態。結果發現陶瓷骨架表面形成數百微米巨孔與許多微孔的結構，經浸泡於模擬體液後，出現浸蝕引起的微孔。各燒結體抗壓強度隨 PVA 添加量增加而降低，隨浸泡時間增加各陶瓷骨架之抗壓強度降低，且重量損失增加。本研究的多孔材料或許可使用在骨缺損修補。

關鍵詞：組織工程、多孔骨架、機械性質、鈣磷酸鹽

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