Preparation and In-vitro Degradation Properties of 3D Printed Nano Silica/Hydroxyapatite/Polylactide Biocomposite

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Abstract. Nano silica/hydroxyapatite/polylactide biocomposite was 3D printed, the effects of the printing conditions on the mechanical properties of the biocomposite were studied and the in-vitro degradation properties of the biocomposite in the PBS solution were tested. The results show that, the best 3D printing conditions are those with the raster angle of 45°, the printing thickness of 0.2mm and the packed density of 100%. In such situations, the nano silica / hydroxyapatite/polylactide biocomposite containing 2% nano silica has the best comprehensive strengths, at which, the tensile, flexural and impact strengths are 85.62MPa, 126.66MPa and 53.56kJ/m² respectively. With the prolong of the in-vitro degradation testing time, the tensile and flexural strengths of the biocomposite will decrease, and the impact strength also decrease generally except at the first one or two weeks for the samples containing 0.2% and 4% hydroxyapatite, more water will be absorbed and more weight will be lost. However, the pH value of the PBS solution is almost kept at around 7.35.

Introduction

Being non-toxic, nonirritant, degradable, biocompatible and easy to be processed, polylactide(PLA) has been successfully used in medical and pharmaceutical areas. It can be used as the material for the born repair, surgical operation suture line and drug delivery, etc.[1-4].

As one of the main inorganic components of the bone of the vertebrates, hydroxyapatite(HA) has good biocompatibility and bioactivity, it can be used as the inducing factor for the bone, and can be bonded with the bone tightly, so it has been widely used as the substitute implanted material for the bone[3,5-6].

When PLA and HA are complexed together, a vesicular flexible structure may be formed which is good for the auxesis, tissue regeneration and vascularization. At the same time, the acidity from the degraded products of PLA inside body can be buffered with HA. The osteoconduction by HA can provide an ideal growth environment bone cells. So, it may be a potential support material in the bone tissue engineering. However, its mechanical strengths are relatively poor, which should still be improved.

3D printing technology is a new developed processing method for materials, it can be applied to produce the items with any sophisticated structure. Some organ tissues have be successfully 3D printed[2,4,7].

In this article, nano silica(n-SiO₂) is used to strengthen the HA/PLA composite, then the n-SiO₂/HA/PLA composite was 3D printed, and the preparation technology and in-vitro degradation properties of the biocomposite were investigated.
Experimentals

Preparation of the Composite

n-SiO2 (the average particle size is 100 mesh), HA (the average particle size is 120 mesh) and PLA (MFR14g/10min at 210°C and 2.16kg) were weighed by the designed proportions and mixed homogeneously, then the composite filament with an average diameter of (1.75±0.05)mm was prepared.

The three-dimensional plots of the standard specimen for the tensile, the flexural and the impact tests according to Chinese national standards GB/T1040-2006, GB/T9341-2008 and GB/T1043-2008 were drawn and saved as .stl.

The standard samples were formed by 3D printing. The diameter of the nozzle is 0.4mm, the temperature of the nozzle was set at 210°C, and that of the platform is 50°C, the thickness of the outside wall was 1.2mm, and those of the top and the bottom layers were also both 1.2mm, the printing speed was 60mm/min.

In-vitro Degradation Test

The phosphate buffered saline (PBS) with the pH of 7.4 was prepared first, each biocomposite sample was immersed in 10mL PBS solution, the solution with the sample was put into an incubator with the temperature of 37°C, the PBS solution was renewal each week. Five pieces of the biocomposite samples were taken at different stages for mechanical properties, water uptake and mass loss testing.

Properties’ Testing


Water Uptake

The water uptake was calculated by the following equation,

\[ x = \frac{m_w - m_d}{m_d} \times 100\% \]

Where, \( m_w \)-the weight of the wet sample at the designed degradation stage, \( m_d \)-the weight of the original dry sample

Mass Loss

The mass loss was calculated by the following equation,

\[ y = \frac{m_0 - m_d}{m_0} \times 100\% \]

Where, \( m_0 \)-the original weight of the sample, \( m_d \)-the dry weight of the sample after a period of degradation testing.

Results and Discussion

The Effects of 3D Printing Conditions on The Mechanical Properties of The Biocomposite

The effects of the 3D printing conditions on the strengths of the composite are listed in Table 1.
Table 1. The effect of the 3D printing conditions on the mechanical properties of the composite (the mass proportion of n-SiO2,HA and PLA is 2:4:96).

<table>
<thead>
<tr>
<th>No.</th>
<th>raster angle/°</th>
<th>printing thickness/mm</th>
<th>packed density/%</th>
<th>tensile strength/MPa</th>
<th>flexural strength/MPa</th>
<th>impact strength/kJ·m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.1</td>
<td>100</td>
<td>82.36</td>
<td>115.32</td>
<td>48.92</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>0.1</td>
<td>100</td>
<td>84.18</td>
<td>120.84</td>
<td>52.22</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>0.2</td>
<td>100</td>
<td>85.62</td>
<td>122.66</td>
<td>53.56</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>0.2</td>
<td>80</td>
<td>83.26</td>
<td>119.35</td>
<td>51.28</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>0.2</td>
<td>60</td>
<td>80.88</td>
<td>118.62</td>
<td>48.86</td>
</tr>
</tbody>
</table>

It can be seen from Table 1 that, the 3D printed sample with a raster angle of 45° has greater strengths than that of 0°, the difference in the raster angle will lead to the variation of the melting state between neighboring layers in the sample, the results mean that, a raster angle of 45° can make the neighboring layers melt together much better. It is reported in the literatures that, a thicker printing thickness is good for the mechanical properties[8-9], the same conclusion can be drawn in this study, the 3D printed samples with a printing thickness of 0.2mm has greater strengths than that of 0.1mm when the raster angle is kept at 45°; The packed density has also great effects on the mechanical properties of the biocomposite, generally, all the tensile, flexural and impact strengths reduce with the decrease of the packed density.

Based on the results shown above, it can be concluded that, when the raster angle is 45°, the printing thickness is 0.2mm and the packed density is 100%, the 3D printed biocomposite containing 2% n-SiO₂ should have the best comprehensive mechanical properties, where, the tensile, flexural and impact strength is 85.62MPa, 126.66MPa and 53.56kJ/m², respectively.

The In-vitro Degradation Properties of The Composite

Keeping the content of n-SiO₂ in the biocomposite is 2%, various biocomposites listed in Table 2 were prepared and the in-vitro degradation tests were carried out.

Table 2. The components of various biocomposites.

<table>
<thead>
<tr>
<th>symbol</th>
<th>mass percentage component</th>
<th>n-SiO₂</th>
<th>HA</th>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td></td>
<td>2</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>C1</td>
<td></td>
<td>2</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td>2</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>C3</td>
<td></td>
<td>2</td>
<td>6</td>
<td>94</td>
</tr>
</tbody>
</table>

The degradation properties of a composite may be evaluated by the changes in the strength and mass of the sample, the pH value of the buffer solution and the water uptake by the sample. The strengths' changes of various biocomposites with the degradation time are shown in Fig.1.
With the prolong of the degradation time, both the tensile and flexural strength will decrease. Generally, the decrease at the first four weeks happens relatively quickly, after that, it will become slower. The final retention rates of the tensile strengths of C1, C2, C3 and C4 after 12-week-degradation are 80.29%, 82.60%, 81.20% and 83.98% respectively, and those for the flexural strengths are 80.19%, 82.89%, 78.93% and 82.48% respectively. At any stage, the flexural strength of the biocomposite with HA is always greater than that of the composite without HA.

A little different from that of the flexural or tensile strength, the impact strength of the composite except C3 will increase at the first one or two weeks, after that, the impact strength began to reduce. After 12-week-degradation, the impact strength can be remained by 77.85%, 82.76%, 79.55% and 77.34 for C1, C2, C3 and C4 respectively.

The water uptake and mass loss of each biocomposite was illustrated in Fig. 2. Generally, the longer the biocomposite is immersed in PBS solution, the more water it will absorb, and the greater the mass may be lost. The water uptake happens more heavily at the first two weeks, then slow down; when more HA is used, the biocomposite will absorb more water at any degradation stage, the reason may be due to that, as one kind of inorganic material, HA has more polar chemical groups such as hydroxyl on its surface, and so it is much easier to absorb moisture than organic PLA matrix when contacting with PBS solution, at the same time, more
interfaces will exist between HA and PLA when more HA is used, some defaults may certainly exist inevitably, which will also cause the biocomposite to absorb more moisture.

![Graphs showing water uptake and mass loss](attachment:graphs.png)

(a) water uptake  
(b) mass loss

Figure 2. The water uptake and mass loss of the biocomposites with degradation time.

![Graph showing pH value change](attachment:pH_graph.png)

Figure 3. The pH value’s change of PBS solution with degradation time.

Fig.3 shows the variation of pH value of PBS solution containing C2 with the degradation time. From the figure, we learn that, the pH value is almost kept around 7.35, only a little change from the original value of 7.4, as is well known that, when PLA is degraded, lactic acid will be produced which will lead to the reduction of the pH value of PBS solution. However, the HA in the biocomposite is alkaline, it will neutralize the acidity caused by the lactic acid, as a result, the total pH value is kept almost unchanged, which means that the degradation of the biocomposite has little effect on the PBS solution.

**Conclusions**

The 3D printed nano silica/hydroxyapatite/polylactide biocomposite with a raster angle of 45°, a printing thickness of 0.2mm and a packed density of 100% has the best comprehensive mechanical properties. All the strengths of the biocomposite can be remained by about 80% after 12 weeks’ in-vitro degradation test, and the mass loss is less than 2.5%. Besides these, the pH value of the PBS solution is almost kept around 7.35, quite near the original 7.4 during the whole testing. All the results mean that, the biocomposite itself is strong and has little effect on the environment of the PBS solution during its degradation, it may be a potential ideal material for some organ tissue engineering.
Acknowledgement
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References