The characterization of mechanical and surface properties of poly (glycerol–sebacate–lactic acid) during degradation in phosphate buffered saline

Zhi-Jie Suna,*, Lan Wu a, Xi-Li Lua, Zhao-Xu Meng a, Yu-Feng Zheng a, De-Li Dong b

a Center for biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
b Department of Pharmacology, Harbin Medical University; Bio-pharmaceutical Key Laboratory of Heilongjiang Province, Harbin 150081, China

1. Introduction

Poly (glycerol–sebacate) (PGS) is a novel biodegradable material that was designed and synthesized firstly by Robert Langer group in 2002 [1]. Lines of evidences suggested that PGS showed good biocompatibility [2,3] and was widely studied in the field of tissue engineering [4–7]. Compared with poly (DL-lactide-co-glycolide), PGS primarily degrades by surface erosion, which gives a linear degradation profile of mass, preservation of geometry and intact surface, and retention of mechanical strength [8].

Although PGS has these advantages, it is expected that the degradation property of PGS could be controlled so as to well suit the variety of medical applications, for example, in drug delivery system [9] or drug-eluting stents [10]. PGS is polycondensed with glycerol and sebacate. Because lactic acid has both hydroxyl and carboxyl groups, it could be doped into PGS polymer backbone and modified the degradation property of PGS. Based on this hypothesis, we synthesized poly (glycerol–sebacate–lactic acid) (PGSL) with 1:1:0.5 mole ratio of glycerol, sebacate and lactic acid and investigated the degradation property and mechanism of the new polymer.

2. Experiment

2.1. Preparation of polymers

The starting materials used for reaction were sebacic acid (2N purity), glycerol (2N purity), and lactic acid (2N purity). The polymers were prepared with 1:1:0.5 mole ratio of glycerol, sebacate and lactic acid at 150 °C under nitrogen for 6 h; the pressure was then reduced to 40 mTorr gradually and held at 140 °C for 30 h to produce an elastomeric polyester. The polymer wafers which were immersed in phosphate buffer solution (PBS, pH 7.4) and thermostated at 37 °C were sampled on day 0, 5, 15, 30 and named as S1, S2, S3, S4, respectively.

2.2. Characterization of polymers

IR spectroscopy was gotten with FTIR spectrometer (spectrum 100, PerkinElmer, USA). Differential scanning calorimeter (DSC) measurements were performed on a PerkinElmer Diamond DSC at heating rate of 10 °C/min to measure the crystalline temperature ($T_c$) and heat of fusion ($H_c$).
The surface morphologies of samples were visualized with scanning electron microscopy (SEM, XL30, Philips).

The tensile tests were performed with a WDS-5 tensile tester (Changchun, China); the crosshead speed was 10 mm/min. The tensile test specimens had dimensions of 40 mm in length, 5 mm in width and 1.4 mm in thickness.

3. Results and discussion

The chemical structure of PGSL was analyzed by using IR spectrum methods. The wide peaks at 3500 cm$^{-1}$ were of the bonding hydroxyl stretch vibration absorption peaks among the molecules, and the peak intensity of S1–4 tended to increase in sequence. The stretch vibration peaks at 2930, 2850, and 1380 cm$^{-1}$ indicated the methyl groups. The stretch vibration peaks at 1750 cm$^{-1}$ indicated the carbonyl of ester, and the peak intensities of S1–4 tended to decrease in sequence (Fig. 1).

Fig. 2 showed the crystalline part of the DSC curves of PGSL samples and the thermal data were listed in Table 1. As shown, the crystallization temperature ($T_c$) and absolute crystallization enthalpy ($\Delta H_c$) of PGSL tended to decrease with the polymer degradation.

Macroscopically, the PGSL wafers in PBS maintained their geometries throughout the period of 30 days (Fig. 3). Mass loss of the PGSL polymers during degradation was shown in Fig. 4. The maintained geometries and linear mass loss were most likely due to the surface erosion.

As shown in Fig. 5 of the SEM observation, erosion pits on the surface of samples increased gradually from S1 to S3. There was minor erosion crack formation on the surface of S4, which could be attributed to the bulk degradation. So it was suggested that degradation of PGSL were through bulk degradation and surface erosion.

Fig. 6 and Table 2 demonstrated the tensile properties of PGSL. It was apparent that, with PGSL degradation, elastic modulus and tensile strength decreased and then underwent an increasing; meanwhile, elongation at break increased and then decreased.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>-23.79</td>
<td>-17.7</td>
</tr>
<tr>
<td>S2</td>
<td>-24.13</td>
<td>-18.7</td>
</tr>
<tr>
<td>S3</td>
<td>-23.35</td>
<td>-5.4</td>
</tr>
<tr>
<td>S4</td>
<td>-24.36</td>
<td>-9.1</td>
</tr>
</tbody>
</table>

The surface morphologies of samples were visualized with scanning electron microscopy (SEM, XL30, Philips).

**Fig. 1.** IR spectrum of the sampled PGSL.

**Fig. 2.** DSC curves of the sampled PGSL.

**Fig. 3.** Photographs of PGSL samples during degradation in PBS.

**Fig. 4.** Mass loss of PGSL during degradation.

**Fig. 5.**SEM observation of PGSL samples.
These results might be due to the alterations of the densities of ester bonds and the ratio of soft and hard segments. The relative decrease of elongation at break of S4 might be as a result of the minor cracks on the surface.

4. Conclusions

Degradation of poly (glycerol–sebacate–lactic acid) (PGSL) was through the bulk degradation and surface erosion. The elastic modulus, tensile strength and elongation at breakage of PGSL were correlative to the period of degradation.

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References