Electrospinning of Biodegradable Polyester Urethane: Effect of Polymer-Solution Conductivity

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This work deals with an investigation of fabrications of nanofibres based on biodegradable polylactic-acid/polyethylene-glycol-chain-linked copolymers, using the electrospinning technique. Crucial attention is paid to describing the effect of polymer-solution conductivity on the morphology of the resulting nanofibres. Nanofibre systems were studied with scanning electron microscopy and the subsequent image analysis of nanofibre diameters. Hydrolytical degradability of the investigated copolymers was studied using gel permeation chromatography. The results show a significant effect of polymer-solution conductivity on the quality of nanofibres.

Keywords: electrospinning, nanofibres, polylactide polyethylene glycol copolymer

1 INTRODUCTION

Electrospinning products based on biodegradable polymers have been suitable materials for innovative tissue-engineering applications.1 Polylactic acid (PLA) is a biodegradable thermoplastic polymer with good properties and processability. Nevertheless, its properties can also be limiting in some of the applications.2 An effective way of how to improve the PLA properties can be a modification of synthesis using a chain-linking reaction.3 In this two-step process, a functionalized low-molecular-weight prepolymer is prepared first and then, in the second step, the chain linking through the reactive chain ends with a chain-linking agent (usually disocyanate) is carried out.4

The research presented here focuses on the electrospinning of polyester urethane (PEU) based on PLA/polyethylene glycol (PEG) copolymer chain linked with disocyanates. The morphology and characteristics of the prepared nanofibres are correlated with the conductivity of the polymer solution. Degradability of the studied PEU was studied under abiotic conditions in a phosphate-buffer medium.

2 EXPERIMENTAL PART

2.1 Materials

L-lactic acid, poly(ethylene glycol) (PEG, $M_W = 400$), hexamethylene disocyanate (HMDI) and Tin(II)$_2$-
ethylhexanoate Sn(Oct)2 (92.5–100.0 %) were purchased from Sigma-Aldrich; phosphate buffer (PB, 0.1 mol.L–1, pH = 7, NaH2PO4 adjusted with NaOH) and tetrahydrofuran (HPLC-grade) were sourced from Chromspec, Brno, Czech Republic.

The synthesis of copolymers was conducted through a polycondensation reaction and, in the second step, a chain-linking reaction with hexamethylene diisocyanate (HMDI) was performed (Figure 1). In this study, a copolymer with a molar ratio of NCO and OH groups equal to 3.2 was used. The preparation of the studied PEU is described in detail in our previous work.5

2.2 Method

The molecular weight of PEU was examined with gel permeation chromatography under the conditions described in reference.4 A hydrolysis test was performed on round-shaped samples (a diameter of 3.4 mm and a thickness of 1.5 mm) fully immersed in a liquid-buffer medium (pH = 7) at 37 °C and 55 °C.

The electrospinning process was carried out on an in-house constructed apparatus consisting of a jet and a target with a separation distance of 18 cm at 23 °C. The PEU solution (12 % of the mass fraction in DMF) was charged with DC 75 kV. The flow rate of the polymer solution was 0.086 mL min–1. The conductivity of the polymer solution was adjusted with citric acid and sodium tetraborate (3:1, w/w) to 59.5, 107.9 and 150.9 μS cm–1.

The morphology of the electrospun nanofibres was studied with scanning electron microscopy (Tescan Vega II LMU, Czech Republic). The morphology analysis of the nanofibres was carried out with an image analysis of SEM micrographs using the ImageJ software.

3 RESULTS

The values of the average molecular weight ($M_w$) of the studied PEU and their reduction during the degradation process at 37 °C and 55 °C are presented in Table 1. While $M_w$ of PEU at the beginning of the degradation experiment was 300 kg.mol–1, the samples showed a 99 % $M_w$ reduction after 25 d.

**Table 1:** Molecular-weight loss of PLA-PEG copolymers during the degradation experiment

<table>
<thead>
<tr>
<th>Degradation time (days)</th>
<th>$M_w$ (kg mol–1)</th>
<th>55 °C</th>
<th>37 °C</th>
<th>$M_w$ (kg mol–1)</th>
<th>55 °C</th>
<th>37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>9.2</td>
<td>300</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>5.6</td>
<td>143</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>8.0</td>
<td>5.1</td>
<td>84</td>
<td>6.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2.3</td>
<td>3.2</td>
<td>3.0</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2.0</td>
<td>2.8</td>
<td>1.9</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>not detected</td>
<td>not detected</td>
<td>1.0</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diameter distributions of the nanofibre systems prepared from the PEU solutions with various conductivity values, together with inserted SEM micrographs, can be seen in Figure 2. Table 2 presents the number ($D_n$), the weight average ($D_w$) and the polydispersity ($D_w/D_n$) of nanofibre diameters.

**Table 2:** Effect of PEU-solution conductivity on the fibre diameter

<table>
<thead>
<tr>
<th>Conductivity (μS cm–1)</th>
<th>$D_n$ (μm)</th>
<th>$D_w$ (μm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.5</td>
<td>0.24</td>
<td>0.36</td>
<td>1.50</td>
</tr>
<tr>
<td>107.9</td>
<td>0.18</td>
<td>0.28</td>
<td>1.55</td>
</tr>
<tr>
<td>150.9</td>
<td>0.29</td>
<td>0.42</td>
<td>1.42</td>
</tr>
</tbody>
</table>

**Figure 2:** Histogram of PEU fibre-diameter distribution and corresponding SEM micrographs (inserted). The conductivity of PEU solutions was adjusted to: a) 59.5 μS cm–1, b) 107.9 μS cm–1 and c) 150.9 μS cm–1.

**Slika 2:** Histogram razporeditve premera REU-vlaken in njihov SEM-posnetek. Prevodnost PEU raztopine je bila uravnana na: a) 59.5 μS cm–1, b) 107.9 μS cm–1 in c) 150.9 μS cm–1.
4 DISCUSSION

The degradation behaviour of PEU is in accordance with the already published results. The kinetics of the $M_n$ reduction is interesting as it is strongly dependent on the temperature. A significantly faster degradation of PEU occurs at a temperature (55 °C) that is close to the glass-transition temperature. On the other hand, the degradation rate observed at 37 °C provides results comparable with the PLA-based polymers. The homogeneity of the electrospun PEU nanofibres was enhanced by increasing the conductivity of the polymer solution, unlike in the case of low-conductivity PEU solutions where an occurrence of the inhomogeneity of the electrospun products was observed. A combination of nano- and sub-microfibres was obtained for the PEU solutions with the lowest (59.5 μS cm$^{-1}$) and the highest conductivity (150.9 μS cm$^{-1}$) while a relatively narrow distribution of nanofibre diameters was found for the PEU solution with a medium conductivity (107.9 μS cm$^{-1}$). The non-uniformity of fibre diameters could have been caused by a broad molecular-weight distribution, whose relation to the fibre distribution was reported in the work of J. Lyons et al., though for a different type of material.

5 CONCLUSIONS

Biodegradable PEU nanofibres based on PLA/PEG chain-linked copolymers can be easily fabricated using the electrospinning process. The morphology of the resulting nanofibres can be significantly influenced by adjusting the polymer solution before the electrospinning process. PEU can provide a product with a mixture of nano- and sub-microfibres that can be potentially useful for specific filtration applications.

Acknowledgements

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