

Original article

Synthesis and characterization of a new biodegradable polyurethanes with good mechanical properties



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ABSTRACT

In the paper, a new biodegradable polyurethane (PU, PU-I) was prepared: the prepolymer was synthesized via bulk ring-opening polymerization with poly(ethylene glycol) ($M_n = 600$) (PEG600) as an initiator and L-lactide (L-LA), ϵ -caprolactone (CL) as monomers, and the prepolymer was chain-extended with an isocyanate-terminated urethane triblock (macrodiisocyanate) to prepare the PU. The macrodiisocyanate, prepolymer and PUs were characterized by ^1H NMR, ^{13}C NMR, FT-IR, high resolution mass spectrometry (HR-MS), gel permeation chromatography (GPC), thermo gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The corresponding PU films showed excellent mechanical properties with a tensile strength of 27.5 MPa and an elongation at break of 996%, and also maintained mechanical properties in physiological saline at 37 °C for more than three weeks, which appeared to be more suitable for biomedical applications.

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1. Introduction

Polyurethanes (PUs) usually exhibit good mechanical properties and desirable blood compatibility, which are considered to be important characteristics for biomedical materials [1–4]. For these advantages, PUs have been widely used in meniscal reconstruction [5], hemostatic sponge [6], vascular prosthesis [7] and artificial skin [8]. However, most commercially available PUs contain aromatic diphenylmethane diisocyanate (MDI) [9–11]. It is known that PUs based on MDI produce mutagenic and carcinogenic substances on degradation [12,13]. In order to overcome this shortcoming, aliphatic diisocyanates are used to prepare PUs which only release non-toxic products on degradation. 1,4-Butanediisocyanate (BDI) is the optimal choice for its high chemical reactivity [14,15], but BDI is prohibitively expensive. 1,6-Hexanediisocyanate (HDI) is much cheaper than BDI and has medium chemical reactivity, but the PUs exhibit mechanical properties unsatisfactory for medical applications when HDI is used as the chain extender [16,17]. The development of biomedical

PUs with good mechanical properties and low cost is therefore highly desirable [18,19].

In this work, we wish to present new aliphatic PUs with low cost for biomedical applications. The prepolymer of poly(ϵ -caprolactone-co-L-lactic acid)-poly(ethylene glycol)-poly(ϵ -caprolactone-co-L-lactic acid) (PCLL-PEG-PCLL) was synthesized via bulk ring-opening polymerization with PEG600 as an initiator and L-lactide (L-LA), ϵ -caprolactone (CL) as monomers. Then, the prepolymer was chain-extended with an isocyanate-terminated urethane triblock to obtain the PUs. The corresponding PU films containing long uniform-size hard segments had higher tensile strength than PU films extended with HDI and were more suitable for biomedical applications.

2. Experimental

2.1. Synthesis of prepolymer (PCLL-PEG-PCLL)

21.5 g (0.15 mol) L-LA was mixed with 21.5 g (0.19 mol) CL in a 100 mL vacuum flask under nitrogen atmosphere, 30.0 g (0.05 mol) PEG600 and 70 mg stannous octoate was added as initiator and catalyst, respectively. The mixture was polymerized under reduced pressure at 140 °C for 24 h. ^1H NMR showed complete conversion.

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^1H NMR (400 MHz, CDCl_3): δ 5.16 (q, $\text{CH}_3\text{-CH-}$), 4.13 (m, $-\text{COO-CH}_2\text{-}$), 3.65 (m, CH_2 of PEG), 2.34 (m, $-\text{OOC-CH}_2\text{-}$), 1.44–1.57 (br, $\text{CH}_3\text{-}$, $-\text{COO-CH}_2\text{-CH}_2\text{-}$, $-\text{OOC-CH}_2\text{-CH}_2\text{-}$), 1.41 (m, $-\text{OOC-(CH}_2)_2\text{-CH}_2\text{-}$). GPC (THF): $M_{w\text{-GPC}} = 1698$, $M_{n\text{-GPC}} = 1464$, $M_{w\text{-GPC}}/M_{n\text{-GPC}} = 1.16$.

2.2. Synthesis of macrodiisocyanate chain extender

1,6-Hexanediisocyanate-1,4-butanediol-1,6-hexanediisocyanate (HDI-BDO-HDI) was prepared by reaction of BDO with eight-fold excess of HDI at 80°C for 3 h without catalyst. After cooling to room temperature, the reaction mixture was washed three times by dry hexane to remove excess HDI. The product was dried at 45°C under reduced pressure, yielding the HDI-BDO-HDI (88%) as a white powder.

^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 7.06 (t, 2H, $-\text{NH-}$), 3.93 (t, 4H, $-\text{COO-CH}_2\text{-}$), 3.33 (t, 4H, $\text{OCN-CH}_2\text{-}$), 2.95 (t, 4H, $-\text{NH-CH}_2\text{-}$), 1.52–1.56 (m, 8H, $-\text{COO-CH}_2\text{-CH}_2\text{-}$, $-\text{NH-CH}_2\text{-CH}_2\text{-}$), 1.39 (m, 4H, $\text{OCN-CH}_2\text{-CH}_2\text{-}$), 1.28 (m, 4H, $\text{OCN-(CH}_2)_2\text{-CH}_2\text{-}$). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$): δ 156.2 ($-\text{NH-CO-}$), 121.5 (OCN-), 63.1 ($-\text{COO-CH}_2\text{-}$), 42.4 ($\text{OCN-CH}_2\text{-}$), 40.0 ($-\text{NH-CH}_2\text{-}$), 30.6 ($\text{OCN-CH}_2\text{-CH}_2\text{-}$), 29.3 ($-\text{NH-CH}_2\text{-CH}_2\text{-}$), 25.4–25.9 ($\text{OCN-(CH}_2)_2\text{-CH}_2\text{-}$, $\text{OCN-(CH}_2)_3\text{-CH}_2\text{-}$, $-\text{COO-CH}_2\text{-CH}_2\text{-}$). HR-MS (m/z): 449.24 [$\text{M}+\text{Na}^+$].

2.3. Preparation of PUs

The chain extender of HDI-BDO-HDI was dissolved in dimethyl sulfoxide (DMSO) at 80°C to get a 25 wt% solution, and the solution was added dropwise into the prepolymer under vigorous mechanical stirring (molar ratio of $-\text{NCO}/-\text{OH}$ was 1.05). When the reaction mixture became viscous, a small amount of DMSO was added to keep the system homogeneous. After the addition was complete, the reaction mixture was stirred at 90°C for about 3.5 h until the NCO peak (2270 cm^{-1}) disappeared in the FT-IR spectrum, and subsequently diluted to a concentration of about 5 wt% solution. The polymer (PU-I) was precipitated in water and dried to constant mass at 35°C under reduced pressure. The chemical structure of PU-I was shown in Scheme 1.

For the purpose of comparison, PU-II was prepared with the same process except using HDI as chain extender.

IR (KBr, cm^{-1}) for PU-I and PU-II: ν_{max} 3319 (N–H), 2933, 2863 (C–H), 1730, 1687 (C=O), 1195, 1092 (C–O). GPC (THF) for PU-I: $M_{w\text{-GPC}} = 147,000$, $M_{n\text{-GPC}} = 107,300$, $M_{w\text{-GPC}}/M_{n\text{-GPC}} = 1.37$. GPC (THF) for PU-II: $M_{w\text{-GPC}} = 82,600$, $M_{n\text{-GPC}} = 66,600$, $M_{w\text{-GPC}}/M_{n\text{-GPC}} = 1.24$.

2.4. Polymer films

The PUs were dissolved in chloroform at room temperature under magnetic stirring for 3 h. Then the solution was poured into a polytetrafluoroethylene (PTFE) mold. The solvent was removed by natural volatilizing at room temperature for two days and subsequently transferred to a vacuum drying oven for one day so as to remove the last traces of solvent under reduced pressure.

3. Results and discussion

3.1. Polymer synthesis

The PCLL-PEG-PCLL copolymers were synthesized via bulk ring-opening polymerization with stannous octoate as catalyst. The ^1H

NMR spectral peaks of the copolymers appearing at δ 5.16, δ 4.13 and δ 3.65 ppm are attributed to the $-\text{CH}$ of LA, $\omega\text{-CH}_2$ of CL and $-\text{CH}_2\text{-CH}_2$ of PEG units, respectively. The L-LA/CL molar ratio (1:1.23) could be determined by comparing the intensity of signals at δ 5.16 and δ 4.13 ppm, which matched the initial ratios (1:1.27) of the components used in the polymerization. The number molecular weight ($M_{n\text{-NMR}}$) of the copolymers was estimated by integrating the ^1H NMR signals pertaining to each monomer according to the method established [20]. The $M_{n\text{-NMR}}$ (1438 g/mol) was consistent with the theoretical molecular weight (M_{theo} : 1457 g/mol) and the result of GPC ($M_{n\text{-GPC}}$: 1464 g/mol). All the results indicated the complete ring-opening reaction.

By chain extending the prepolymer (PCLL-PEG-PCLL) with the macrodiisocyanate (HDI-BDO-HDI), the PU-I with well-defined and uniform hard segments (HDI-BDO-HDI) was prepared. The uniformity of the hard segments is known to be extremely important for the mechanical properties. With macrodiisocyanate as chain extender, the PU-I with excellent mechanical properties and high molecular weight could be made.

3.2. Thermal transition

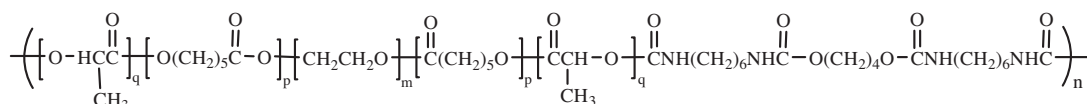
Fig. 1 shows the DSC thermograms of the PU films which were measured with a DSC2910 (Universal, USA) at a heating rate of $10^\circ\text{C}/\text{min}$ from -50°C to 150°C under N_2 (30 mL/min). Two glass transition temperatures ($T_{g1} = -40.2^\circ\text{C}$, $T_{g2} = 62.4^\circ\text{C}$) could be observed in the thermogram of PU-I extended with macrodiisocyanate, which corresponded to the soft ether segments and hard urethane segments, respectively. Because of the uniform longer hard segments contained in the PU, the hard phase was hardly miscible with the soft phase in the linear PU, which resulted in micro-phase separation and two clearly T_g being observed [21]. PU-II extended with HDI contains no long hard segments, as such it has only one T_g (-42.8°C) and no phase separation, as observed in the thermogram. In addition, no exothermic peaks in the thermograms of either PU indicated that PU-I and PU-II were amorphous.

3.3. Thermal stability

Fig. 2 shows the TG and DTG analysis of the PU films, which were heated at $20^\circ\text{C}/\text{min}$ from 50°C to 600°C under air atmosphere (40 mL/min) with a TGA 2050 analyzer (Universal, USA) [22]. The PU-I and PU-II showed mass loss distributed in two steps. The first weight loss occurred at around $256\text{--}354^\circ\text{C}$ (PU-I: 68 wt%, Fig. 2a) and $250\text{--}364^\circ\text{C}$ (PU-II: 63 wt%, Fig. 2b) which was the decomposition of urethane and ester bonds in PUs. In the temperature region at around $354\text{--}456^\circ\text{C}$ (Fig. 2a) and $364\text{--}461^\circ\text{C}$ (Fig. 2b), the ether bonds decomposed almost completely, and the observed mass loss of 31 wt% and 36 wt% were consistent with the PEG content in PU-I (31.8 wt%) and PU-II (36.8 wt%), respectively. The TG curves of films having no obvious difference indicated that the PU-I and PU-II had similar thermal stability.

3.4. Mechanical properties

The mechanical properties of the PU films were measured with a single-column tensile test machine (Model HY939C, Hengyu Instruments, Ltd, Dongguan, China) at the cross-head speed of $50\text{ mm}/\text{min}$ according to the national standard GB/T1040-2006.



Scheme 1. The chemical structure of PU-I.

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