Polymer Degradation and Stability 137 (2017) 216–228

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

The influence of the length of the degradable segment on the functional properties and hydrolytic stability of multi-component polyurethane elastomeric films

Milena Špírková*, Jiří Hodan, Libor Kobera, Jana Kredatusová, Dana Kubies, Luďka Machová, Rafał Poręba, Magdalena Serkis, Alexander Zhigunov, Jiří Kotek

Institute of Macromolecular Chemistry AS CR (IMC), Heyrovsky Sq.2, 16206 Prague 6, Czechia

ARTICLE INFO

Article history:
Received 3 November 2016
Received in revised form
20 January 2017
Accepted 31 January 2017
Available online 1 February 2017

Keywords:
Polyurethane elastomer
Lactide
Hydrolytic degradation
Mechanical properties
Thermal properties
Surface analysis

ABSTRACT

The hydrolytic degradation of aliphatic polyurethane (PU) films made from polycarbonate-based macrodiol (MD), diisocyanate-1,6-hexane, butane-1,4-diol (BD) and D,L-lactide-based oligomeric diol (DLL) was studied. The influence of the length of DLL was tested in phosphate-buffered saline (PBS) for periods of up to 12 months. One macrodiol (molecular weight ~2000 Da), three DLL oligomers (~400, 660 and 850 Da) and three MD-to-BD-to-DLL molar ratios were chosen for the PU synthesis. The isocyanate-to-total hydroxyl-group ratio was kept constant at 1.05. The functional properties of raw polyurethane films and samples immersed for 1, 3, 6, 9 and 12 months in a model physiological environment (37 °C, pH = 7.4) were studied from the segmental to the macroscopic level. Tensile testing and water uptake experiments, as well as differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (XRD) analyses, were used for the characterization of the raw and PBS-treated films. The study shows that the length of the DLL chain is much more important for functional PU properties than the mass content of DLL in the PU film. The incorporation of the shortest DLL into the PU backbone leads to a degradable PU material with outstanding tensile properties when not subjected to the hydrolytic treatment. However, the incorporation of oligomers with longer DLL chains results in PU materials with substantially deteriorated tensile characteristics due to more pronounced phase separation compared to systems without DLL or with the shortest DLL. The degradability of the PU films can be controlled to a relatively broad extent by altering DLL content and length. The investigation of functional properties of new PU materials during the hydrolytic process under physiology-mimicking conditions is important for potential medical/package coating/film applications.

1. Introduction

Polyurethanes (PUs), which are commercial polymers with very broad versatility, have been used in medicine for several decades [1]. Their preferred use is as robust and long-term stable biomaterials for the fabrication of catheters and vascular grafts and for biomedical devices and implants [1–3]. Current demands mainly require the development of efficient biodegradable or bioresorbable materials with short or limited lifetimes [4–9].

The popularity of thermoplastic polyurethanes (TPUs) in practice is based on two main advantages: (i) simple modification of the polyurethane composition and preparation procedure leads to targeted functional properties; and (ii) available technological techniques (such as casting, spraying, extrusion and injection) enable the preparation of TPU products with complicated shapes and of various sizes. TPUs exhibit excellent tensile properties, owing to the segmental character of TPUs. TPUs are linear block copolymers containing soft and hard segments. While the stiffness and strength are due to the hard segments, the extensibility depends on the soft segments. The thermodynamic incompatibility between the soft and hard segments results in the phase separation that (together with the PU composition, domain structure, and interaction between the segments inside and between the domains) plays a key role in PU properties [10–13].

* Corresponding author.
E-mail address: spirkova@imc.cas.cz (M. Špírková).

http://dx.doi.org/10.1016/j.polymdegradstab.2017.01.021
0141-3910/

Although PUs and their blends and nanocomposites have previously been employed in tissue engineering as implants and scaffolds, as well as in drug delivery [1–3,5,6,8,13,14], they are also intensively studied from the point of view of further potential applications in medicine [15–20]. The safe use of biomaterials with suitable lifetimes in biomedicine or as packing materials requires knowledge of their stabilities/degradabilities, in addition to detailed information on their functional properties. Stability testing of new materials can be performed under substantially different conditions with respect to temperature and chemical or physical stimuli, and different property changes (chemical, flame, hydrolytic, oxidative, irradiation, etc.) can be measured over different time spans [14,16–18,21–23]. For new biomaterials that are intended for use in medical applications, long-term experiments (time of exposure from weeks up to several years) under simulated physiological conditions (phosphate buffered saline at pH 7.4 and usually a temperature of 37 °C) are intensively used for hydrolytic stability tests [17,22,24–29].

Unlike polyether- and polyester-based macrodiols, polycarbonate (PC)-based PUs belong to a relatively new class of PU elastomeric systems. The first PUs prepared from commercially available PC macrodiols were based solely on aromatic diisocyanates [21,30–32]. Two main practical reasons—better stability to oxygen and UV radiation and lower toxicity of degradation products (compared to PUs made from aromatic diisocyanates) [6,9,32,33]—led to the use of aliphatic or cycloaliphatic diisocyanates in PC-PU formulations [27–29,34–42].

Polylactide and polylactid acid (PLA), which are biodegradable, compostable, and biocompatible thermoplastic polymeric materials derived from renewable resources [43–45], are widely used materials, as well. They have been used extensively in biomedical materials, disposable plastics and packing materials [46,47]. However, their mechanical properties are limited (stiff and brittle material, tendency towards physical ageing), which reduces their applicability [48]. Common processes for overcoming this drawback are copolymerizing lactide compounds with other monomers or macromolecules to obtain flexible lactide-based copolymers [22,23,26], or PLA blending, e.g., with polyurethanes [23,49–51]. However, the immiscibility of most of the blends requires the use of additional substances (compatibilizers) to improve compatibility.

This contribution is an ongoing part of our long-term research, with the ultimate goal being the synthesis of controllably degradable materials that could be used in biomedical applications. Polycarbonate-based PUs containing lactide-based linkers in the backbone can fulfil this demand. The current study confirmed the high hydrolytic stability of the three-component PUs [28] with the preservation of their excellent mechanical properties for up to two years. The idea of regularly incorporating small amounts of short degradable units (based on D,L-lactide derivatives) into the PU backbone was found to be a very effective tool for the acceleration of the hydrolytic degradation process. In a previous paper, we tested an oligomeric diol (DLL) containing, on average, two lactide units in the chain [29]. Unlike hydrolytically stable three-component TPUs, these four-component TPU elastomeric films feature controlled lifetimes under simulated physiological conditions [29]. This fact stimulated the preparation of additional DLL oligomers containing on average four or six lactide units in the chain, followed by their build-up into the PU backbone, which is presented in this paper. The multi-scale characterization of the four-component PU films (containing macrodiol, diisocyanate, chain extender and oligomeric DLL diol) was concentrated on the influence of the contents, regularity and localization of degradable ester units in the PU material on functional properties, which were tested before and after hydrolytic process. Although the detailed characterization concentrated on four-component systems containing longer DLL diols, when necessary, selected results on PUs, published recently in Refs. [28,29], are discussed in this paper, as well.

2. Experimental

2.1. Materials

The commercially available polycarbonate-based macrodiol, T4672 (number-average molar mass $\langle M_n \rangle$ = 2770 g mol^{-1}, dispersity $Đ_M$ = 3.20, T_g = - 49 °C) was kindly provided by Asahi Casei Co., Japan. The 1,6-diisocyanatohexane (HDI), butane-1,4-diol (BD) and dibutyltin dilaurate (DBTDL) were purchased from Fluka. Three oligomeric D,L-lactide-based diols (D1 to D3) were synthesized. The synthesis of D1 is described elsewhere [39]. D2 and D3 were prepared in the same manner; only the molar ratio BD-to-D,L-lactide was changed (see 2nd column in Table 1). The descriptions and the basic characterization of the D1 to D3 oligomers are given in Table 1 and ^{1}H NMR spectra are shown in Fig. 1.

A schematic representation of the structures forming the PU chain is shown in Fig. 2.

As follows from Fig. 2, T4672 polycarbonate-based macrodiol (sequence ***M***) is composed of solely *even* methylene –CH_2- units and it thus exhibits substantial regularity and rigidity. The

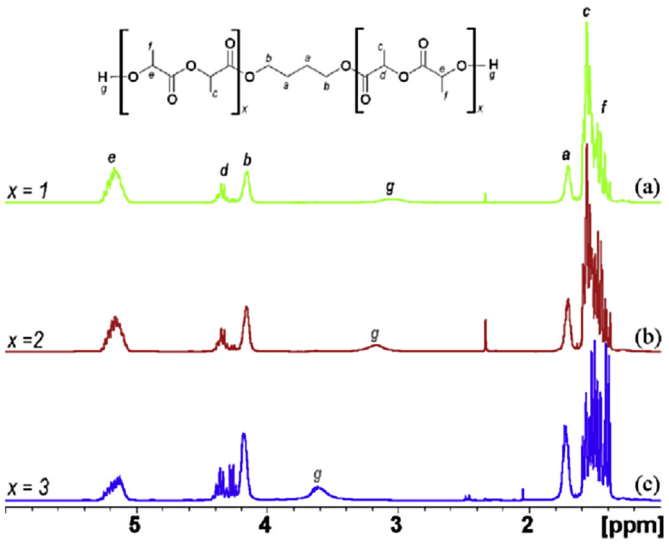

Fig. 1. ^{1}H NMR spectra of lactide-based diols D1 (x = 1), D2 (x = 2) and D3(x = 3).

Table 1
Codes and characteristics of D,L-lactide-based diols Dn.

DLL code	[BD] to [lactide] molar ratio	Theoretical molar mass g.mol^{-1}	Average molar mass (^{1}H NMR) g.mol^{-1}	Average number of ester unit per Dn chain	T_g from DSC°C
D1	1: 2	378	399	4.3	–37
D2	1: 4	666	657	7.9	–19
D3	1: 6	954	851	10.6	–8