



# Experimental study of the simulated process of degradation of polycarbonate- and D,L-lactide-based polyurethane elastomers under conditions mimicking the physiological environment



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## ABSTRACT

The extent of the hydrolytic degradation of aliphatic polyurethane (PU) films made from polycarbonate-based aliphatic macrodiol (MD), diisocyanate-1,6-hexane, butane-1,4-diol (BD) and D,L-lactide-based oligomeric diol (DLL) was tested in phosphate-buffered saline (PBS) for a period of up to 12 months. Two macrodiols of equal molecular weight (~2000 Da), differing in chain composition and regularity, and equal 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 four-component 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 up to the macroscopic level. Tensile testing and water uptake experiments, as well as DSC, SEM, AFM, FTIR and WAXD analyses, were used for the comprehensive characterization of the raw and PBS-treated films. The study shows that the untreated four-component PU films are highly elastomeric materials with very high tensile strength and suitable thermal properties for potential medical coating/film applications. The DLL oligomeric diol turned out to be a very efficiently degradable unit, leading to substantial mechanical property deterioration. The products of more regular macrodiol have higher tendency to the degradation process; 89% or 94% of the original toughness value is lost in just 12 months of immersion. The studied type of PU can be practically used either as fairly stable high-performance elastomers for short-term applications (up to 3 months) or as degradable materials, when the time of exposure to the physiology-mimicking conditions is sufficient.

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## 1. Introduction

Polyurethanes have been used in medicine for several decades [1–8], but the purposes of their utilization have changed during this long period of time. The first PUs were applied as robust and long-term stable biomaterials for the fabrication of catheters, vascular grafts, biomedical devices and implants [2,3,5–7]. However, current demands require the development of efficient biodegradable or bioresorbable materials with short or limited lifetimes [8–14].

Thermoplastic polyurethanes (TPUs) represent a very popular and important part of polyurethane industrial products, even though they are not produced in such high quantities as PU foams.

TPUs have two main advantages as follows: (i) targeted functional properties can be achieved relatively easily by modification of the polyurethane composition and preparation procedure, and (ii) various sizes and complicated shapes of TPU products can be obtained by casting, extrusion, injection or spraying techniques. TPUs exhibit excellent mechanical properties due to their advantageous combination of elasticity and flexibility together with high strength and Young's modulus. The simplicity of their recycling is a further positive criterion of their utility. Although PUs and their blends and nanocomposites have previously been employed in tissue engineering, as scaffolds, and in drug delivery [7,10,15–21], they are still amply studied from the point of view of further potential applications in medicine [13,22–24]. The safe use of biomaterials with required lifetimes in biomedicine requires not only detailed information on their end-use properties but also the knowledge of their stability/degradability.

The functional properties of TPUs depend, in addition to other

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factors, on their content of hard and soft segments, length, and spatial arrangement (intermixing or phase separation), which can be tuned by the choice of starting compounds (isocyanate, macrodiol and chain extender), reaction mixture composition, preparation protocol, and thermal history [25]. Therefore, the relationship between the composition, structure and properties, which will provide comprehensive descriptions of the mechanical, surface, thermal, swelling and other properties, has to be studied for each new PU system in detail.

In general, stability tests can be conducted from substantially different viewpoints (i.e., under different conditions, such as temperature, and exposure to different chemical and physical stimuli), with the aim of investigating different properties (e.g., thermal, oxidative, chemical, irradiation, flame, and hydrolysis) and on very different time scales. The conditions for the practical hydrolytic degradation/stability tests of various polymeric and composite materials are chosen individually according to the intended use, and they substantially differ in the temperature, time and environment of their sample exposures [5,8,14,15,26–38]. Long-term experiments under physiologically simulated conditions are essential for the assessment of the hydrolytic stability of new biomaterials to be used in medical applications [26,28,29,31,36,37,39].

Polycarbonate-based PUs belong to a relatively new class of PU elastomeric systems. The first PUs prepared from commercially available macrodiols were based solely on aromatic diisocyanates [33,34,40,41]. The use of aliphatic or cycloaliphatic diisocyanates in PU formulations [8,42–50] has become more popular for two main reasons, better stability during exposure to oxygen and UV radiation and lower degradation product toxicity than the use of aromatic-based diisocyanates [10,13,29,41].

In the present contribution, the preparation of TPU elastomeric films with a controlled lifetime in simulated physiological conditions is described. This study is a part of our long-term research, with the ultimate goal of the synthesis of controllably degradable materials that could find use in biomedical applications. Recently, we have examined the hydrolytic stability of PUs made from polycarbonate-based macrodiol, diisocyanate-1,6-hexane and butane-1,4-diol under model physiological conditions. The study confirmed the high hydrolytic stability of the three-component PUs with the preservation of their excellent mechanical properties for up to one year [50]. The use of this reaction mixture for the preparation of degradable PUs seems to be counterproductive for the first view. However, the idea of incorporating small amounts of short degradable units into the PU backbone [51] was the stimulus and motivation for the present study. As the lactide-based derivatives are efficient degradable materials [39,51,52,53], we prepared an oligomeric D,L-lactide-based diol (DLL) containing, on average, two lactide units in the chain [45]. The conditions of the preparation and multi-scale characterization of the four-component PU films (containing, in addition to macrodiol, diisocyanate, chain extender and oligomeric DLL diol in the PU backbone) have been recently published [45,46].

The role of the polycarbonate-based diol is the formation of elastomeric TPU with excellent mechanical properties, whereas DLL is a hydrolytically degradable component built-up into the polyurethane backbone. Degradable ester units are thus regularly distributed in each PU chain and, hence, in the PU film. We believe that this setting could be more efficient for the hydrolytic degradation process compared with the currently popular mixing or blending of degradable lactide-based material into the polyurethane matrix [1,12,19,22,24,26].

The end-use properties of three- and four-component aliphatic TPUs were recently studied in detail on the segmental to macroscopic levels [42–47]. However, no degradation tests under physiologically simulated conditions have been performed thus far on

PU systems containing DLL units. This paper is the continuation and extension of the degradation studies investigating the efficiency of DLL in the hydrolytic degradation process of four-component PUs [50].

## 2. Experimental

### 2.1. Materials

Two commercially available polycarbonate-based macrodiols, T4672 (marked as “T4”, number-average molar mass  $\langle M_n \rangle = 2770 \text{ g mol}^{-1}$ , dispersity  $D_M = 3.20$ ) and T5652 (marked as “T5”, number-average molar mass  $\langle M_n \rangle = 2874 \text{ g mol}^{-1}$ , dispersity  $D_M = 3.23$ ), which were kindly provided by Asahi Casei Co., Japan, as well as butane-1,4-diol (BD), dibutyltin dilaurate (DBTDL) and 1,6-diisocyanatohexane (HDI, all from Fluka), were used. The synthesis and detailed characterization of oligomeric D,L-lactide-based diol (DL-L) are described elsewhere [45]. A schematic representation of the structures forming the PU chain is shown in Fig. 1.

As the T4672 polycarbonate-based macrodiol contains only *even* methylene  $-\text{CH}_2-$  units, it exhibits higher regularity and higher rigidity. On the other hand, T5652 contains *even* and *odd* methylene  $-\text{CH}_2-$  units at an *equal* molar ratio and is therefore characterized by a higher irregularity and higher flexibility compared with T4672, as shown previously [44]. Both macrodiols contain, on average, approximately  $23 \pm 4$  carbonate groups per chain. DLL contains, on average, 4 degradable ester units, distributed relatively regularly in the oligomeric diol (See Fig. 1).

#### 2.1.1. Preparation procedure

All PU films were prepared by a one-step procedure. Prior to the reaction, all components were thoroughly mixed in dried acetone to obtain a homogenous solution that was subsequently poured into the Teflon forms. After solvent evaporation at room temperature, the Teflon moulds were placed in an oven in a nitrogen atmosphere. The equimolar ratios of the hydroxyl groups of macrodiol (MD = T4672 or T5652), BD and DLL used for PU film preparation were chosen on the basis of our previous studies [45,46]. All reactions proceeded in bulk at  $90^\circ\text{C}$  for 24 h in the presence of the organotin catalyst DBTDL at very low concentration (50 ppm/mol of urethane groups) at constant  $r$  and  $R$  ratios ( $r = [\text{NCO}]/[\text{OH}]_{\text{total}} = 1.05$ , where  $[\text{OH}]_{\text{total}} = [\text{OH}]_{\text{MD}} + [\text{OH}]_{\text{BD}} + [\text{OH}]_{\text{DLL}}$ ), and  $R = [\text{OH}]_{\text{MD}} = [\text{OH}]_{\text{BD}} = [\text{OH}]_{\text{DLL}} = 1$ . The final thickness of the films was  $250 \pm 25 \mu\text{m}$ . Individual sample codes and compositions are summarized in Table 1, 1st and 2nd columns. As the previous study revealed that the oligomeric DLL diol belongs to the soft-segment component [46], the hard-segment content (HSC, Table 1, 3rd column) was calculated as the weight percentage of BD and HDI with respect to the total mass of all reagents used.

The PU films were subsequently either measured by the set of analytical methods (raw samples) or cut into individual pieces and placed in a glass degradation flask. Degradation proceeded in the phosphate-buffered saline solution (PBS)<sup>1</sup> with an additional 0.02 wt% of sodium azide  $\text{NaN}_3$  at  $37^\circ\text{C}$  for 1, 3, 6, 9 and 12 months. Whereas the buffer environment and temperature were the same, the specimen shape differed according to the method of analysis as follows: (a) dumbbell-shaped samples for tensile properties and rectangular samples for the microscopy analyses were cut from the PU film and fixed to custom-built PE frames prepared for this purpose in IMC, and (b) pieces of PU films for water uptake and DSC analyses were fixed on an inert thread. Both types of immersion

<sup>1</sup> PBS – Phosphate-Buffered Saline contains monobasic potassium phosphate, sodium chloride, and dibasic sodium phosphate.

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