



Biostability of polyurethanes. Study from the viewpoint of microphase separated structure



L. Rueda, B. Fernandez d'Arlas, M.A. Corcuera, A. Eceiza*

Materials + Technologies' Group, Department of Chemical and Environmental Engineering, Polytechnic School, University of the Basque Country, Pza. Europa 1, 20018 Donostia – San Sebastián, Spain

ARTICLE INFO

Article history:

Received 8 December 2013

Received in revised form

9 June 2014

Accepted 21 June 2014

Available online 28 June 2014

Keywords:

Hydrolytic degradation

Segmented thermoplastic polyurethane

Microphase separated structure

Hydrogen bonding

Hard segment

ABSTRACT

The materials design focused on biomedical applications involves the analysis under physiological simulated conditions because it is of prime importance the determination of life-time and reliability of these materials. The goal of this work were the study of the biostability of a series of segmented thermoplastic polyurethane elastomers (STPUE), containing PTHF and PCL blocks as soft segment (SS), by means of hydrolytic degradation tests for 3 years to determine the useful life-time. Physico-chemical and thermal properties were analyzed from the viewpoint of microdomain structure. The results suggested a reorganization in hard and soft segment ordered structure by means of a greater number of hydrogen bonds which contributed to phase separation and hence low-water uptake, being less susceptible to hydrolytic attack.

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1. Introduction

Biomedical applications of polyurethanes (PU) go back to the early 1960s when polyesterurethane foam was used for in situ bone fixation, while polyesterurethane coatings were applied to cardiovascular implants [1]. Since then, a certain controversy in the use of these materials was created due to the premature degradation of the polymer depending on the reactants used in the synthesis. Subsequent experiments also showed no tumor induction in response to the material. A later study developed by Boretos et al. [2] further confirmed the use of PU as potential biomaterials, performing particularly well in cardiovascular applications. At that moment, numerous researchers oriented their studies to produce several polyurethane formulations using different starting materials to increase the life-time in polyurethanes, confirming that these elastomeric materials are considered as one of the most attractive in biomedical devices [3], even though they have been found to degrade in vivo via hydrolysis, oxidation and stress cracking [4].

Nowadays, thermoplastic polyurethanes are considered to be one of the most biocompatible and haemocompatible materials currently available, and their excellent physical–mechanical

properties allows for the incorporation of bioactive molecules. In addition, make them popular choices in the manufacture of biomedical devices such as the left ventricular assist device, endotracheal tubes, catheters and vascular grafts [5].

Segmented thermoplastic elastomeric polyurethanes (STPUE) are versatile polymeric matrices typically constructed alternating soft (SS) and hard segments (HS). It is well known that the properties of polyurethanes are remarkably affected by these segments (in terms of content, type or nature and molecular weight) and whose thermodynamic incompatibility, drives the polymer system into a nano/microphase separation.

On the other hand, the materials design focused on biomedical applications involves the analysis under physiological simulated conditions due to the demand of obtaining possible candidates as biodegradable and bioadsorbible materials [6]. In this way, it is of prime importance the determination of life-time and reliability of these materials and tries to get a progressive material degradation at the same time as the formation or replace of new tissue/organ [7], for example. Permeability of biomaterials to water and air can potentially lead to problems in implanted devices [8], so it will be necessary to establish considerations regarding the development of the right standards for the use of useful materials both on a short-term, as on a long-term basis [9].

In this work, a series of STPUE containing PTHF and PCL blocks as soft segment (SS) were synthesized. It is worth noting that polyester block as PCL, susceptible to hydrolysis, represents a critical

* Corresponding author. Tel.: +34 943017185; fax: +34 943017130.

E-mail addresses: arantxa.eceiza@ehu.es, iapexmea@ehu.es (A. Eceiza).

point in these materials biostability [10,11]. However, PCL is a very useful polymer in medical applications and the life-time of PCL polymer has been estimated higher than 2 years [10]. For this reason, from the perspective of polyurethane use in biomedical devices, it is crucially important to analyze the biodegradability of these materials. In this way, human physiological conditions can facilitate hydrolytic degradation [12]. Taking it into account, the biostability of the materials used in this work was evaluated by means of hydrolytic degradation tests to determine the useful life-time or hydration time without loss in final polyurethane properties, which are analyzed from the viewpoint of microdomains structure. The objective of this study was to provide a comprehensive image of the domain structure within these polyurethanes and then attempt to rationalize their potential for hydrolytic degradation based on the knowledge of the structure.

2. Materials and methods

2.1. Segmented thermoplastic elastomeric polyurethanes

STPUE was synthesized by using a 2332 g/mol block copolymer (polycaprolactone-*b*-polytetrahydrofuran-*b*-polycaprolactone) diol (PCL-*b*-PTHF-*b*-PCL) from Sigma–Aldrich, 1,6-hexamethylene diisocyanate (HDI) kindly supplied by Bayer and 1,4-butanediol (1,4-BD) from Fluka, as chain extender. A two step polymerization was employed to synthesize STPUEs containing 18, 25, 32 and 42 wt% of hard segment whose components were combined as can be seen in Table 1 and coded as follow: STPUE-18, STPUE-25, STPUE-32 and STPUE-42. Firstly, the isocyanate-terminated prepolymer was prepared by reaction between the polydiol and diisocyanate at 100 °C for 12 h in nitrogen atmosphere. Then, 1,4-BD was added at the same temperature during 5 min with vigorous stirring. Finally, the viscous mixture was transferred into a mold and kept in a vacuum oven at 100 °C for 24 h. The synthesis and characterization of this type of matrix was detailed elsewhere [13].

3. Experimental part

3.1. Hydrolytic degradation study

Hydrolytic degradation tests were carried out using STPUE films prepared by compression molding in a hydraulic press and whose diameter was 8 mm and thickness 100 μm. Several films of each known weight dried polyurethane sample were immersed in phosphate buffer solution (PBS) with a solution/sample relation of 45:1, in according to the procedure explained in literature [14,15]. Tests were performed at 37 °C constant temperature oven. Three vials of each sample were taken out at different intervals of three months for 3 years. At each time point, the samples were rinsed several times with deionized water, surfaces were blotted using filter paper and were weighed immediately using an analytical balance to evaluate the water uptake. After that, samples were dried in a desiccator until constant mass to evaluate the influence of hydration time and hydrolytic degradation on polyurethanes by means of changes in microstructure and properties.

Table 1

Molar ratio, hard segment content and designation of the synthesized polyurethanes.

Polyurethane	Molar ratio PCL- <i>b</i> -PTHF- <i>b</i> -PCL:HDI:1,4-BD	Hard segment (% HS content)
STPUE-18	1:2:1	18
STPUE-25	1:3:2	25
STPUE-32	1:4:3	32
STPUE-42	1:6:5	42

The percentage weight gain (sorption) of the samples was calculated as:

$$\text{Sorption}(\%) = (M_t - M_i)/M_i * 100 \quad (1)$$

where M_t is swelled weight and M_i is the initial weight of sample. Average of three independent readings was reported for each specimen.

On the other hand, degradation rates were characterized by weight loss measurements, which were calculated as follows:

$$\text{Weight loss}(\%) = [(w_i - w_d)/w_i] \times 100 \quad (2)$$

where w_i and w_d , are the weight of films before and after degradation tests, respectively.

3.2. Polyurethane characterizations

A Perkin–Elmer LC-295 gel permeation chromatography (GPC) equipment was used for the determination of molecular weight, with a Perkin–Elmer LC-30 RI refractive index detector. Four Phenogel GPC columns, from Phenomenex, with 5 μm particle size and 10⁵, 10³, 100 and 50 Å porosities respectively were used. 1 mL/min of tetrahydrofuran (THF) was used as mobile phase. Polyurethane solutions were filtered using nylon filters of 0.45 μm pore dimension and 20 μL of solution was injected. M_n and M_w , number and weight average molecular weights, respectively, calculated by universal calibration, are referred to polystyrene standards (monodisperse patterns). Polydispersity index (PI) was defined as M_w/M_n ratio.

DSC scans were recorded on a Mettler Toledo 822e instrument. Temperature and heat flow were calibrated using an indium standard. Samples (3–5 mg) were subjected to different scans from –60 °C to 180 °C at 10 °C/min under N₂ atmosphere.

ATR-IR was performed using a Nicolet Nexus 670 FT-IR spectrometer equipped with a single horizontal Golden Gate ATR cell. Spectra were recorded using a spectral width range from 600 to 4000 cm⁻¹, with 2 cm⁻¹ resolution and an accumulation of 20 scans.

TGA was performed at a scanning rate of 10 °C/min from 25 to 600 °C, under N₂ atmosphere using a TGA/SDTA 851 Mettler Toledo instrument.

4. Results and discussion

Table 2 shows weight and number average molecular weight as well as polydispersity index calculated by GPC in starting materials and after 3 years of hydrolytic degradation tests. As can be seen, synthesized polyurethanes did not show significant differences in molecular weight. Moreover, the absorption humidity percentages in films as well as the loss in weight were analyzed by water uptake tests for 3 years. The water uptake is an indirect measurement of hydrophilic character in materials [6]. In this way, polyurethanes with high SS content showed lower hydrophilic behavior along test time, in agreement to WCA results showed previously [13].

Table 2

Weight average molar mass, number average molar mass and polydispersity index of polyurethanes synthesized in bulk.

Sample	\overline{M}_w initial (g/mol)	\overline{M}_w 3 years (g/mol)	\overline{M}_n initial (g/mol)	\overline{M}_n 3 years (g/mol)	PI _{initial}	PI _{3years}
STPUE-18	2.1 × 10 ⁵	2.0 × 10 ⁵	1.3 × 10 ⁵	1.1 × 10 ⁵	1.6	1.9
STPUE-25	1.1 × 10 ⁵	1.6 × 10 ⁵	6.4 × 10 ⁴	5.6 × 10 ⁴	1.7	2.8
STPUE-32	6.1 × 10 ⁴	4.4 × 10 ⁴	3.3 × 10 ⁴	2.4 × 10 ⁴	1.8	1.9
STPUE-42	3.0 × 10 ⁴	2.7 × 10 ⁴	1.7 × 10 ⁴	1.5 × 10 ⁴	1.8	1.8

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