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Shape-memory properties of crosslinked biobased polyurethanes

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ABSTRACT

Biobased crosslinked polyurethanes were synthesized and characterized as shape-memory polymers. Both the macrodiol and the diisocyanate were derived from renewable sources; the first one from castor oil, and the second one from L-lysine amino acid. The influence of component molar ratios, crosslink density and maximum elongation on the shape-memory properties was analyzed. The thermal analysis showed that polyurethanes were microphase separated. Though the study of the shape-memory properties, it was seen that shape-memory was influenced by crosslink density. A higher crosslink density led to a greater shape recovery, since crosslinks are the responsible for memorizing the shape of the material. With the increase of maximum elongation, both shape fixity and recovery decreased due to higher amount of crosslink net points were broken. Moreover, the synthesized polyurethanes showed its potential to be used in biomedical applications, according to the preliminary *in vitro* cytotoxicity assays.

1. Introduction

The development of shape-memory polymers (SMPs) has drawn increasing attention among smart materials in the last years, due to SMPs can find broad applications in different sectors ranging from the aerospace to the biomedical [1–7]. These kind of smart materials are able to remember their original shape after being deformed and recover it as a response to an external stimulus, being heat the most common [8,9]. In general, the physical (crystalline segregated domains or entanglements) or chemical crosslink (covalent bonding) of thermoresponsive polymers are the responsible for memorizing the shape [10,11]. While the so-called switching phase serves as a molecular switch and enables the fixation of the temporary shape [12,13] showing a transition temperature (T_{trans}), which can either be a glass transition (T_g) or a melting temperature (T_m). During the shape-memory test the material is heated and deformed in a temperature above the T_{trans}, named as switching temperature (T_s), and it is subsequently quench at a temperature below T_{trans} in order to fix the shape. Once the sample is reheated above T_{trans} its original shape is restored [14]. Shape-memory properties are dependent on the morphology, the degree of microphase separation and the conditions at which the tests were carried out [13,15]. In addition, in chemically

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crosslinked SMPs the crosslink density also influences on shape-memory properties, due to it determines the relative motion of segments and net points, and hence the capability of the polymer to recover to its original shape after being deformed [8]. Moreover, in materials with a broad thermal transition, the so-called temperature-memory effect (TME) takes place, when the temperature at which the deformation is applied is within the range of the thermal transition [16–20].

Segmented polyurethanes are one of the most noteworthy SMPs [9,21–24], due to their versatility, which enables the synthesis of materials with different properties just by manipulating their composition. Segmented polyurethanes are block copolymers composed by two blocks, one formed by a macrodiol (polyether or polyester diol), and the other composed by a diisocyanate and a low molecular weight chain extender or crosslinker [25,26]. The incompatibility between both segments leads to microphase separation which depends on block lengths, hydrogen bonding and crystallization extent [27,28].

Furthermore, because of economic, environmental and social concerns the interest the synthesis of shape-memory polyurethanes based on components derived from renewable sources is gaining attention. In most of the works, only the polyol is biobased and the diisocyanate used is based on fossil sources [29–31]. Nevertheless, in a recently published work [32] we successfully synthesized biobased thermoresponsive linear thermoplastic polyurethanes, using a macrodiol derived from castor oil, a L-lysine amino acid based diisocyanate and a diol type chain extender derived from corn sugar. Since it was seen that covalently crosslinked polyurethanes show better thermal, thermomechanical and shape-memory properties than linear polyurethanes [33,34], in this work chemically crosslinked polyurethanes were synthesized, using the same macrodiol and diisocyanate employed previously [32]. As crosslinker the 1,1,1-tris-(hydroxymethyl)propane (TMP) with primary hydroxyl groups was employed.

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used in order to establish the transition temperatures of the thermally-responsive polyurethanes. Furthermore, in order to analyze physicochemical properties of the material Fourier transform infrared spectroscopy (FTIR) was used. The mechanical properties of the synthesized polyurethanes were analyzed by performing tensile and Shore D hardness tests. In the same way, the study of thermally-activated shape-memory properties was carried out by means of thermo-mechanical cyclic test. Finally, preliminary evaluation of the *in vitro* cytotoxicity and surface properties were also estimated.

2. Experimental

2.1. Materials

Poly(butylene sebacate)diol derived from castor oil, with a number-average molecular weight of 3505 g mol^{-1} and a hydroxyl index of 32.01 determined by titration with ASTM D 4274-88 Test Method A [35] was used as macrodiol. Ethyl ester L-lysine diisocyanate (226 g mol^{-1}) and 1,1,1-tris-(hydroxymethyl)propane (134.17 g mol^{-1}) crosslinker were supplied by CHEMOS GmBH and Fluka, respectively. The macrodiol was dried under vacuum for 6 h at 80 °C prior to use. The chemical structures of the macrodiol, diisocyanate and crosslinker are shown in Fig. 1.

2.2. Synthesis of the polyurethanes

Polyurethanes were synthesized by two step bulk polymerization procedure. The reaction was carried out in a 250 mL five-necked round-bottom flask equipped with a mechanical stirrer and dry nitrogen inlet. Firstly, dried polyol and diisocyanate were placed in the flask and heated in a thermo-regulated silicon bath at 100 °C for 5 h. Then, the crosslinker was added to the prepolymer at 100 °C and the mixture was rapidly stirred for 10–15 min. Finally the resulting viscous liquid was quickly poured between two Teflon® coated metal plates separated by 1.5 mm and pressed at 100 °C under 50 bar for 10 h. The NCO to OH groups molar ratio of all polyurethanes was kept constant at 1.01. Designation, macrodiol/LDI/TMP molar ratios and LDI/TMP segment content of the polyurethanes are shown in Table 1. As a reference pure LDI/TMP segment (PUTMP 100) was also synthesized.

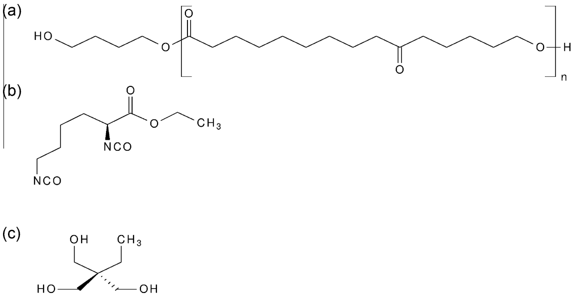

Fig. 1. Structure of the different materials used in the synthesis: poly(butylene sebacate)diol (a), ethyl ester L-lysine diisocyanate (b) and 1,1,1-tris-(hydroxymethyl)propane (c).