



Design of fully aliphatic multiblock poly(ester urethane)s displaying thermoplastic elastomeric properties



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ABSTRACT

By the combination of prepolymers with very different physical/chemical properties, better performance materials can be obtained. In the present study, three hydroxyl-terminated fully aliphatic polyesters have been chain extended to prepare new multiblock poly(ester urethane)s (PEU) displaying thermoplastic elastomeric characteristics. Poly(butylene succinate), poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate), and poly(neopentyl glycol adipate) have been respectively used as soft-hard, hard and soft segment. The evaluation of molecular, thermal, and mechanical properties and hydrolytic degradation profile permitted to correlate the behavior of the so-obtained materials with their molecular structure, and highlighted that it is possible to nicely tune the final characteristics of this class of PEUs by just varying the mutual amount of the three segments.

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1. Introduction

Polymers are among the most used materials, due to their ease of synthesis, low cost and versatility. About 300 Mt of plastics are annually produced around the world to be used for a wide variety of applications ranging from packaging to automotive, furniture, clothes and so on [1]. Nevertheless, the need for high performance materials to be employed in specific market niches is constantly increasing.

On the other hand, the growing environmental concern, due to the dramatic aquatic and terrestrial pollution, is driving industrial and academic research toward the synthesis of biodegradable and bio-based polymers. Similarly, the adoption of hydrolytically degradable polymers in biomedicine, especially for tissue engineering and controlled drug release is demanded, as it can permit to overcome some of the major issues related to these applications

(i.e. surgical removal of the implant) [2].

In this framework, aliphatic polyesters play an important role, thanks to their promising physical/mechanical properties and proven biodegradability and biocompatibility [3,4]. Moreover, various monomers, such as succinic acid, adipic acid, butanediol and lactic acid can be prepared from renewable resources, allowing the preparation of fully bio-based materials [5–7]. In the last two decades, aliphatic polyesters (APs) have been extensively studied and are nowadays produced in large scale: Bionolle™, Ecoflex®, Ecovio®, Ingeo™ and Mater-Bi® are some of the most well-known examples of industrial products based on aliphatic polyesters.

Unfortunately, even though very interesting, APs cannot satisfy the requirements for all the different applications where hydrolytic and/or enzymatic degradation is necessary [8].

Copolymerization represents therefore the most used way to modulate the polymer properties. However, by the introduction of a significant amount of one (or more) comonomeric unit along the polymer backbone, a substantial decrease of the melting temperature is usually observed [9–11].

In addition, as it is well known, the achievement of high molecular weight polymers by polycondensation of dicarboxylic esters

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and diols is somehow troublesome.

Chain extension is a well-established synthetic strategy which can help to overcome these issues. In particular, the use of diisocyanates has been deeply investigated [12–15]. By reacting diisocyanates with hydroxyl-terminated polyesters, high molecular weight poly(ester urethane)s (PEU), can be easily achieved. Moreover, by selecting the number, chemical structure and relative amount of the hydroxyl-terminated polyesters, it is possible to synthesize a wide plethora of new materials with tailored and more functional properties, according to the intended final use.

With the aim of designing hydrolytically degradable strong, elastic and flexible multiblock polyesters, three different hydroxyl terminated prepolymers have been considered: poly(butylene succinate) (PBS–OH), poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate) (PCCE–OH), and poly(neopentyl glycol adipate) (PNA–OH) (Fig. 1).

PBS has been chosen as semicrystalline soft-hard segment, as it displays $T_g < T_{room} < T_m$. On the other hand, PCCE will confer rigidity to the system, since it appears as a glassy amorphous material ($T_g > T_{room}$), while PNA has been selected as the soft segment, because it possesses T_g well below T_{room} and T_m close to T_{room} , and therefore will bestow an increased flexibility.

Finally, hexamethylene diisocyanate (HDI) is used with the purpose of coupling together the OH-terminated polyesters and of achieving higher molecular weights. Moreover, to preserve hydrolytic and enzymatic degradability a high concentration of ester groups is necessary. Therefore, the percentage of HDI in the final polymer remains quite low (below 5 wt%).

Other PBS-based poly(ester urethane)s have been reported in the literature but, to the best of our knowledge, this is the first time that three segments with so different physical/chemical properties have been coupled together to nicely tailor the behavior of the final materials and to obtain a new class of fully aliphatic thermoplastic elastomers.

It is also worth noticing that most of the monomers employed in the syntheses can be obtained either from renewable resources or fossil fuels [5,6,16,17].

The effect of the relative amount of PBS, PCCE and PNA on the physical/mechanical properties and hydrolytic degradation behavior of the final material has been deeply investigated and linked to the chemical structure of the polymers.

Mechanical properties of the freshly synthesized poly(ester urethane)s have been measured by tensile tests to rupture and cyclic tensile tests. Moreover, the hydrolysis rate has been verified by degradation experiments under physiological conditions (37 °C and pH 7.4).

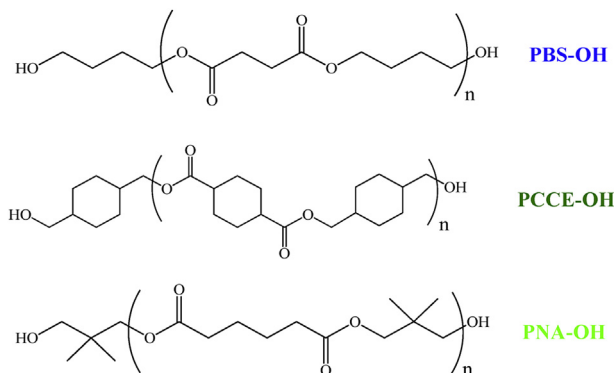


Fig. 1. Chemical structures of the hydroxyl terminated prepolymers employed in the synthesis of the PEUs.

2. Material and methods

2.1. Materials

Succinic acid (SA), adipic acid (AA), 1,4-cyclohexanedicarboxylic acid (CHDA), neopentyl glycol (NPG), 1,4-butanediol (BD), 1,4-cyclohexanedimethanol (CHDM), titanium tetrabutoxide (Ti(OBu)₄) and hexamethylene diisocyanate (HDI) (Sigma–Aldrich) were reagent grade products; SA, AA, CHDA, NPG, BD, CHDM and HDI were used as supplied, whereas Ti(OBu)₄ was distilled before use.

2.2. Synthesis of hydroxyl-terminated prepolymers

Hydroxyl-terminated PBS, PNA and PCCE were respectively synthesized by reacting SA with BD, NPG with AA, and CHDA with CHDM. In all cases, 50% molar excess of diol was considered with respect to dicarboxylic acid content.

All reactions were carried out in bulk employing titanium tetrabutoxide as catalyst (about 150 ppm of Ti/g of polymer) in a 200 ml glass reactor; temperature and torque were continuously recorded during polymerization. The prepolymers were obtained according to the usual two-stage polymerization procedure. In the first stage, under pure nitrogen flow, the temperature was set at 180 °C and kept constant until more than 90% of the theoretical amount of water was distilled off (about 90 min). In the second stage the pressure was progressively reduced to 0.1 mbar, in order to facilitate the removal of the excess of glycol, and the temperature was risen to 220 °C. The syntheses were stopped after two additional hours (Torque increase of 2–3 Ncm with respect to the value measured at the beginning of the second stage).

The prepolymers obtained were carefully purified by dissolution in chloroform and precipitation in methanol. The samples were then kept under vacuum at room temperature for at least one week to remove the residual solvent.

2.3. Synthesis of multiblock polymers

Chain extension reactions were accomplished in bulk at 170 °C under nitrogen atmosphere, by adding hexamethylene diisocyanate (HDI) to the molten prepolymers. The reactions were carried out until a constant torque was measured (about 1 h). An equimolar amount of isocyanate groups with respect to the OH terminal groups concentration in the prepolymers was considered. After the chain extension process, the PEUs have been purified by dissolution in chloroform and precipitation in methanol. Multiblock copolymers were prepared by chain extending PBS–OH with different mass percentages of PNA–OH and PCCE–OH. According to the scheme reported in Figure S1, four different multiblock copolymers have been therefore obtained: PBS₅₀PCCE₅₀, PBS₅₀PCCE₃₀PNA₂₀, PBS₅₀PCCE₁₀PNA₄₀ and PBS₅₀PNA₅₀. Subscript values indicate the relative percentage of each block in the poly(ester urethane) (the exact weight percentage of each segment is indicated in Table 2). Chain extended PBS homopolymer was also considered for sake of comparison.

2.4. Film preparation

Films of about 200 μm thickness were obtained by compression moulding the polymers between two Teflon plates, with an appropriate spacer, at a temperature $T = T_m + 40$ °C for 2 min under a pressure of 2 ton/m² (Carver C12, laboratory press).

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