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Hydrolysable PBS-based poly(ester urethane)s thermoplastic elastomers

M. Fabbri [a], M. Gigli [b], R. Gamberini [a], N. Lotti [b,*], M. Gazzano [c], B. Rimini [a], A. Munari [b]

[a] Department of Sciences and Methods for Engineering, University of Modena and Reggio Emilia, Italy
[b] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Italy
[c] Organic Synthesis and Photoreactivity Institute, CNR, Bologna, Italy

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A B S T R A C T

In this contribution a new class of aliphatic poly(butylene succinate) (PBS)-based poly(ester urethane)s has been synthesized and characterized from the molecular, thermal and mechanical point of view. Hydrolytic degradation studies under physiological conditions have been conducted to assess their biodegradation rate. To obtain copolymers showing both thermoplastic and elastomeric properties, the chain-linking strategy has been considered. In particular, two hydroxyl-terminated oligomers have been synthesized by melt polycondensation: poly(butylene succinate) (PBS), as a “hard segment”, and two poly(butylene adipate/diglycolate) P(BAmBDGn) random copolymers as a “soft segment”. The introduction of ether-linkages along the PBA chain permitted to depress its crystallinity degree and to enhance the wettability. Multiblock copolymers were finally obtained by chain extending with hexamethylene diisocyanate each P(BAmBDGn) copolymer with two different mass percentages of PBS: 30% and 50%. All copolymers maintained good thermal stability and were characterized by melting temperatures above 100 °C. Elastic modulus (E) and stress at break (σ_b) varied with the chemical composition: the higher the PBS amount, the higher E and σ_b. No yield and very high elongations at break were observed. Hydrolytic degradation studies highlighted an increase of the degradation rate with the increase of the BDG content.

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1. Introduction

Biodegradable polymers are employed in a wide range of biomedical applications such as sutures, implants, scaffolds for tissue engineering and devices for controlled drug delivery. This is because they offer a great advantage over other materials: thanks to their reabsorption in the human body, biodegradable polymers permit to avoid the use of invasive medical devices that have to be removed from the patient [1]. Polymers used in biomedics have anyway to follow strict requirements: among all, they have to show high biocompatibility and nontoxic compounds have to be released during the degradation step [2].

In this framework, aliphatic polyesters are the most studied class of biodegradable polymers, because they are readily susceptible to hydrolytic and biological attack [3,4]. Polylactide (PLA), polyglycolide (PGA), poly(ε-caprolactone) (PCL) and their copolymers are already commercially available for biomedical purposes. Unfortunately, although they are well established in clinical practice, the current compositions present different drawbacks [5]: in particular, the mechanical, physicochemical, and biological properties for different applications are not easily tailorable.

Another interesting member of the aliphatic polyester class is poly(butylene succinate) (PBS). PBS is already available on the market under the trade name Bionolle™ (Showa-Denko, Japan) [6] and GS Pla™ (Mitsubishi Chemical, Japan) [7]: currently, its major applications regard mulching films and compostable bags.

Among polycondensates, PBS possesses one of the highest melting temperature, good thermal stability and excellent processability. However, its low biodegradation rate, due to the high crystallinity degree, and the poor mechanical properties, render it not suited for many applications [8]. The most used way to improve PBS properties is undoubtedly the copolymerization strategy: by the introduction of a comonomeric unit, the biodegradation rate and the mechanical properties are modified because of the reduction of the crystallinity degree. Copolymerization of PBS with various co-units has been extensively studied and the influence on the biodegradation rate, besides the physico/chemical and mechanical properties has been reported [9–13].

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* Corresponding author. Tel.: +39 051 2090354; fax: +39 051 2090322.
E-mail address: nadia.lotti@unibo.it (N. Lotti).

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Recently, our group synthesized and characterized different PBS-based copolymers obtained inserting ether and thioether linkages along the PBS backbone via reactive blending or copolycondensation [14–19]. Through this latter procedure, we have been able to modulate the mechanical behaviour as well as the biodegradability of PBS [20,21]. Unfortunately, it suffered of two major drawbacks: the strength of the synthesized polymers decreased and, moreover, their melting temperature collapsed if significant amounts of the comonomeric unit were present.

In addition, as it is well known, the achievement of high molecular weight polymers by polycondensation of dicarboxylic esters and diols is not easy.

To overcome these constraints, the use of chain extenders, such as diisocyanates, could represent a solution [22]. This approach leads to the formation of poly(ester urethane)s (PEU), by simply coupling diisocyanates with hydroxyl-terminated polyesters. Furthermore, by changing the kind and chemical structure of the hydroxyl-terminated polyesters used in the synthesis, it is possible to tailor the final properties of the material according to the desired application.

In this view, in the present research work we present a novel class of PBS-based multiblock PEU. In order to obtain new biodegradable thermoplastic elastomers showing promising mechanical properties and maintaining melting temperatures above 100 °C, a “hard segment” and a “soft” one have been coupled to obtain the new poly(ester urethane)s.

Hydroxyl-terminated PBS has been considered as a hard segment, while two hydroxyl-terminated poly(butylene adipate/diglycolate) (P(BAmBDGn)) random oligomers, containing different molar % of BDG co-units, were synthesized as soft segments.

Other PBS-based poly(ester urethane)s have been reported in the literature [23–28], but to the best of our knowledge, this is the first time that ether-linkages containing PEU have been prepared. In our opinion, the introduction of ether-linkages along the poly(butylene adipate) macromolecular chain should depress the crystallinity degree and should enhance the surface wettability of the obtained polymers, thus their biodegradability should be improved. In addition, we expect that the thermal properties won't be compromised and the mechanical strength and elongation to break will be significantly enhanced.

Lastly, it is worth pointing out that the degradation rate of the synthesized polymers has been tested by subjecting them to hydrolytic degradation experiments under physiological conditions (37 °C and pH 7.4). Therefore, in this contribution, the term biodegradability is used with this specific meaning.

2. Material and methods

2.1. Materials

Succinic acid (SA), adipic acid (AA), diglycolic acid (DGA), 1,4-butanediol (BD), titanium tetrabutoxide ($Ti(OBu)_4$), hexamethylene diisocyanate (HDI) (Aldrich) were reagent grade products; SA, AA, DGA and BD were used as supplied, whereas $Ti(OBu)_4$ was distilled before use.

2.2. Synthesis of hydroxyl-terminated prepolymers

Hydroxyl-terminated PBS (PBS-OH) was synthesized starting from SA and BD, while hydroxyl-terminated poly(butylene adipate/diglycolate) (P(BA*x*BDG*y*)-OH) random copolymers were prepared starting from different ratios AA/DGA (70/30 and 50/50 mol%) and BD. In all cases, 50% BD molar excess was considered with respect to dicarboxylic acids content.

All reactions were carried out in bulk employing titanium tetrabutoxide as a catalyst (about 150 ppm of Ti/g of polymer) in a 200 ml glass reactor, with a thermostated silicon oil bath; temperature and torque were continuously recorded during polymerization. The polymers 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 glycol excess, and the temperature was risen to 230 °C. The syntheses were stopped after two additional hours (Torque increase of 2–3 N cm 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 one week to remove the residual solvent.

2.3. Synthesis of polymers

Chain extension reactions were accomplished in bulk at 160 °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.

Multiblock copolymers were obtained by chain extending each P(BA*x*BDG*y*)-OH random precopolymer with two different mass percentages of PBS-OH: 30% and 50%. Chain extended PBS homopolymer was also considered for sake of comparison.

2.4. Film preparation

Films of $PBS_mP(BAxBDGy)_n$ and of PBS homopolymer 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/m^2 (Carver C12, laboratory press). The obtained films were about 0.2 mm thick.

2.5. Hydroxyl and acid terminal group determination

The OH terminal groups concentration in the prepolymers was determined by titration.

Briefly, 0.6 g of each prepolymer was dissolved in a 1:9 acetic anhydride/pyridine solution and kept at 100 °C under reflux for 1 h. Reaction was stopped by washing with acetone and distilled water. Titrations were run by means of a NaOH 1 M solution using phenolphthalein as indicator.

The COOH terminal groups concentration was obtained using the same procedure, but dissolving the polymer in the solely pyridine. Experiments have been carried out in triplicate and the average values have been considered.

2.6. Molecular characterization

The polymer structure and actual composition were determined by means of ^1H NMR spectroscopy. The samples were dissolved in chloroform-d solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. ^1H NMR spectra were recorded at room temperature for solutions with a polymer concentration of 0.5 wt% (a relaxation delay of 0 s, an acquisition time of 1 s and up to 100 repetitions). The BA and BDG sequence length in P(BA*x*BDG*y*) copolymers was determined by ^{13}C NMR spectroscopy and a confirmation of the statistical arrangement of the comonomeric units in

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