Tailoring poly(butylene 2,5-thiophenedicarboxylate) features by the introduction of adipic acid co-units: Biobased and biodegradable aliphatic/aromatic polyesters

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ABSTRACT

A class of eco-friendly copolyesters based on poly(butylene 2,5-thiophenedicarboxylate) (PBTF) is presented. The main goal of the study was to enhance the biodegradation rate of PBTF homopolymer. To this purpose, aliphatic sequences based on adipic acid have been introduced in the macromolecular backbone. The synthesized polymers have been characterized from thermal and structural point of view and their properties have been compared to those of the two homopolymers, i.e. PBTF and poly(butylene adipate). The peculiar microstructure of PBTF, due to the presence of an uninduced 2D-ordered phase, i.e. *meso*-phase, impacted also the copolymers' behavior, e.g. causing an increase of the materials' stiffness.

Biodegradation rate in compost increased with the increase of mobile aliphatic sequences that allowed for an easier access to the ester bonds by the enzymes responsible for chain depolymerization. Lastly, gas permeability resulted strictly dependent on copolymer composition. Copolymers rich in thiophenedicarboxylate co-units displayed a gas barrier behavior comparable to poly(ethylene furanoate), while with the increase of adipate content the permeability increased, remaining however competitive with respect to that of polyolefines and polylactic acid.

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1. Introduction

The growing concern about aquatic and environmental pollution, together with the depletion of fossil fuel resources, is pulling academic and industrial research toward the design of high performance eco-friendly plastic materials capable of substituting the traditional plastics, especially for the realization of short life-span or disposable items. In this view, bioplastic production is increasing at a considerable rate, as it is expected to grow from the actual 4.2 to 6.1 Mtons/year in 2021 [1]. Among the studied bioplastics, polyesters, whose discovery dates back to the work of Carothers at the beginning of 20th century [2], are probably the most interesting class. Depending on the monomers used, polyesters can be divided into two main categories: aliphatic and aromatic. By coupling aromatic and aliphatic moieties, aromatic/aliphatic copolymers can be also prepared. Copolymerization is indeed one of the best tools to boost the performances of a polymer by coupling the positive characteristics of each comonomeric unit.

In particular, as regards aromatic/aliphatic polyesters, the aromatic fraction confers physical and mechanical stability, while the aliphatic one guarantees the material biodegradability. Moreover, copolymerization itself is a means of enhancing polyester biodegradability, generally owing to a reduced degree of crystallinity of the final materials with respect to the parent homopolymer [3–5].

So far, the most successful example of aliphatic/aromatic copolyester is Ecoflex, developed and commercialized by BASF since the late 90s [6]. Ecoflex is a partially biobased, biodegradable plastic of poly(butylene adipate/terephthate) random copolymers. Due to its very interesting properties, many research groups

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have focused on the synthesis of Ecoflex-like polyesters having a fully-biobased character. In particular, in the last years, with the aim of substituting the terephthalic subunit, polymers based on 2,5-furandicarboxylic acid (FDCA) have received considerable attention, also because of their low gas permeability [7] that rendered poly(ethylene furanoate) (PEF) so far the most credible biobased alternative to PET [8]. As a consequence, also aliphatic/aromatic copolymers of FDCA have been synthesized [9—17].

Recently, we have reported on the synthesis of an aromatic polyester, i.e. poly(butylene 2,5-thiophene dicarboxylate) (PBTF), as a possible *alter ego* of furanoate-based polyesters, given its exceptionally high gas barrier properties [18]. With the purpose of enhancing its biodegradability, in this work we propose the synthesis and characterization of Ecoflex-like copolyesters based on 2,5-thiophenedicarboxylic acid (TFDCA) and adipic acid (AA), namely poly(butylene adipate/2,5-thiophenedicarboxylate)s (P(BAxBTFy).

The combination of the above mentioned dicarboxylic acids with 1,4-butanediol (BD) imparts to the here proposed copolymers a 100% biobased character, as all the raw materials can be obtained from renewable resources. BD can be prepared by hydrogenation of succinic acid [19], while bio-AA is derived from glucaric or muconic acid [20]. Most interestingly, TFDCA is a product of the reaction of adipic acid with thionyl chloride [21,22].

P(BAxBTFy) random copolymers have been prepared by melt polycondensation and characterized from the molecular and thermo/mechanical point of view. Compostability and gas barrier properties have been also considered to provide a full insight into the behaviour of this new class of TFDCA-based polymers.

2. Experimental

2.1. Materials

2,5-thiophenedicarboxylic acid (TFDCA) and adipic acid (AA) were purchased from TCI (Tokyo, Japan). BD, chloroform, methanol and titanium tetrabutoxide (TBT) were obtained from Sigma Aldrich (Saint Louis, MO, USA). TBT was distilled before use.

2.2. Polymer synthesis and film preparation

The synthesis of poly(butylene 2,5-thiophene dicarboxylate) has been reported elsewhere [18].

Poly(butylene adipate) (PBA) and poly(butylene adipate/2,5-thiophene dicarboxylate) copolymers (P(BAxBTFy)) have been synthesized through melt polycondensation, carried out in two steps. A 30% molar excess of 1,4-butanediol with respect to the carboxylic diacid(s) was used and 400 ppm/$g_{polymer}$ of TBT were added to the reaction mixture. In the first step, under nitrogen flux, the temperature was set at 170 °C. The reaction proceeded until more than 90% of the theoretical water produced during esterification was distilled off. At this time point, pressure was gradually reduced to 0.1 mbar and temperature was increased to a maximum of 210 °C (II step). The reaction was completed when constant torque was measured.

The as-synthesized polymers were purified by dissolution in chloroform and subsequent precipitation in methanol. Purified polymers were dried to constant weight under vacuum at 25 °C. Films were obtained by compression moulding in a press (Carver, Wabash, IN, USA). Samples were melted at a temperature equal to $T_m + 40$ °C in the press, then a pressure of 5 tons/m^2 was applied for 2 min. Films were cooled down to room temperature, keeping the pressure applied, by passing tap water through the press plates.

Film thickness was determined by Sample Thickness Tester DM-G (Brugger Feinmechanik GmbH, Munich, Germany). At least three

different measurements, each run on 10 different points of the polymer film surface, were carried out.

2.3. Molecular, thermal and structural characterization

Polymer structure was evaluated by ^{1}H NMR spectroscopy at RT. A Varian Inova 400-MHz was used for the measurements.

Molecular weight and polydispersity index were determined by gel-permeation chromatography (GPC) at 30 °C with a 1100 HPLC system equipped with PLgel 5-μm MiniMIX-C column. A UV-detector was employed. Chloroform was used as eluent with a 0.3 mL/min flow. Molecular weight calibration curve was obtained using polystyrene standards in the range 800—100000 g/mol.

TGA was carried out under nitrogen atmosphere by means of a Perkin Elmer TGA7 apparatus. Gas flow of 30 mL/min and heating scan of 10 °C/min were used for the analysis.

A Perkin Elmer DSC6 was used for calorimetric analyses. Weighed samples were encapsulated in aluminium pans and heated from −60 °C to 190 °C at 20 °C/min (I scan), held there for 3 min, then quenched to −60 °C and reheated from to 190 °C at 20 °C/min (II scan).

To determine the crystallization rate under nonisothermal conditions, the samples were heated at 20 °C/min to about 40 °C above melting temperature, kept there for 3 min and then cooled at 5 °C/min.

Other specific thermal treatments carried out on P(BA30BTF70) copolymer have been described in the text.

X-ray diffraction patterns of polymeric films were performed in the wide angle region using a PANalytical X'PertPro diffractometer equipped with a fast X'Celerator detector. The radiation was supplied by a copper target ($\lambda = 0.1548$ nm) and 567 points at interval 0.1° (2θ) were scanned for 100s each.

2.4. Mechanical characterization

Tensile tests were performed on rectangular films (5 mm wide and 0.2 mm thick) with a crosshead speed of 10 mm/min by using a Instron 4465 tensile testing machine, equipped with a rubber grip and a 100 N load cell. A preload of 1 MPa was applied to each specimen prior to testing. At least five replicates were run and the results are provided as the average ± standard deviation.

2.5. Composting studies

The degradation experiments have been carried out at 58.0 ± 0.1 °C. Mature compost was supplied by HerAmbiente S.p.a. (Bologna, Italy) and had the following composition (as declared by HerAmbiente): organic carbon: 22.08% of the dry solid, humic and fulvic carbon: 13.44% of the dry solid, C/N ratio: 12.97, pH: 8.15 and salinity: 2.88 dS/m. Weighed film specimens of about 20 × 20 mm were employed. Each sample was placed in a 100 mL bottle in between two layers of compost (20 g each). On top of the second layer, 10 mL of deionized water were added. Specimens were withdrawn from the compost at determined time intervals, washed accordingly to the procedure previously described [23], and dried over P_2O_5 under vacuum to constant weight. The weight loss was then calculated using the following equation:

$$((m_i - m_f)/m_i) * 100 \tag{1}$$

where m_f and m_i are the final and the initial sample weight, respectively.

Surface microstructure was analysed by scanning electron microscopy (SEM) on gold sputtered films glued with carbon tape on aluminium stabs on a Philips 515 instrument (Amsterdam, The