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Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT) and their blends upon melt processing

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Poly(lactic acid) (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT) are biodegradable aliphatic polyesters, which being semicrystalline and thermoplastic can be processed by conventional methods. Their blends give interesting materials for industrial packaging applications, due to their increased ductility as PBAT content increases. However, like many aliphatic polyesters, the PLA matrix degrades upon melt processing thus affecting the thermo-mechanical features of the blended material. In this work, we studied the effect of processing at high temperature on the molecular weight distribution, morphology, and thermo-mechanical properties of both homopolymers, as well as the PLA/PBAT 75/25 blend. Notably, different processing conditions were adopted in terms of temperature (range 150–200 °C) and other relevant processing parameters (moisture removal and nitrogen atmosphere). Analysis of PLA/PBAT blends indicated that intermolecular chain reactions took place under strong degradative conditions of PLA, yielding PLA/PBAT mixed chains (copolymers). Increasing amounts of copolymers resulted in improved phase dispersion and increased ductility, as SEM and mechanical tests indicated. Conversely, reduced PLA degradation with less copolymer formation, afforded higher modulus materials, owing to poorer dispersion of the soft phase (PBAT) into the PLA matrix.

1. Introduction

Recently, poly(lactic acid) (PLA) became a polymer of large interest not only in the traditional areas of biomedical and pharmaceutical applications but also in the commodity area, i.e. mainly packaging applications. Indeed PLA has biodegradability, annually renewable availability, and processability following standard melt processes such as injection moulding, film blowing or melt spinning [1]. Different approaches were investigated to tailor the thermo-mechanical properties of the final material, among which has to be mentioned copolymerization with other lactones [2,3] or functionalized lactides [4–6] and lactones [7,8].

However, in a perspective of production scale-up, melt blending of PLA with elastomeric polymers (soft component) (e.g.: poly(ε-caprolactone) [9], poly(hydroxybutyrate) [10], poly(butylene succinate) [11], and poly(butylene adipate-*co*-terephthalate) [12]) appears a sustainable effective approach to improve the thermo-mechanical behaviour of PLA-based materials, while maintaining the biodegradability [13].

Likewise many aliphatic polyesters, however, PLA is reported to degrade during thermal processing or under hydrolytic conditions, giving a rapid reduction of molecular weight that affects the final properties of the material, such as the mechanical strength [13,14]. A great mass of data indicates that the thermal degradation of PLA is due to a random main-chain scission reaction [15], as well as depolymerization [16], oxidative degradation [15], and trans-esterification reactions [16]. Moreover, reactive end groups, residual catalyst, unreacted starting monomer, and other impurities have been reported to enhance the PLA thermal degradation [16]. Commonly, efforts are aimed at the suppression of the polymer degradation in the melt [17].

Here we propose a different approach that considers the degradative behaviour of PLA upon melt processing as a key factor to rationalize and manipulate morphology, and thermo-mechanical features of PLA-based blends through molecular weight size and distribution. Therefore, we will show how the processing at increasing temperatures and in different experimental conditions can be used to modulate the structural, morphological, thermal and mechanical features of PLA/PBAT blends, using the behaviour of pure PLA and PBAT processed under the same conditions as reference.

2. Experimental

2.1. Processing of materials

PLA2002D (Cargill Dow) (PLA) and EcoflexFBX7011 (BASF) (PBAT) were processed in a Brabender plastograph mixer

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(OHG47055, 30 cm^3) at 150, 170, 190 and 200 °C, blade rate 50 rpm, mixing time 10 min, starting from 41 g of crude material. For dried samples (sample_d), pre-weighed polymer amounts were dried for 2 h under reduced pressure (0.01 mbar) at 60 °C. For blends prepared under nitrogen flow (sample_N), a nitrogen flow (around 300 ml/min) was applied and kept constant during the entire process. For dried samples processed under nitrogen (sample_dN), both the previous procedures were applied. In all cases, final torques are the torques (Nm) registered at the process end, while specific mechanical energy (SME) was evaluated as the full integral, melting peak included, of the registered torque curve. Materials were stored at room temperature after processing.

2.2. Preparation of PLA/PBAT blends

PLA2002D (Cargill Dow) (PLA) and EcoflexFBX7011 (BASF) (PBAT) were processed in a Brabender plastograph mixer (OHG47055, 30 cm^3) at 150 and 200 °C, blade rate 50 rpm, mixing time 10 min, starting from 41 g of crude materials. The same procedures as previously described for the processing of pure materials were applied for the preparation of the blends under different processing conditions (sample_d, sample_N, sample_dN). Blends were stored at room temperature after processing.

2.3. Characterization of materials

Thermogravimetric analysis (TGA) measurements were performed on 10–15 mg polymer samples either under nitrogen atmosphere or under air with a Mettler Toledo TGA/SDTA 851 thermobalance. Samples were heated from 30 to 600 °C at 10 °C/min. T_d is the onset decomposition temperature, evaluated as 5% weight loss; WR_{600} is the mass residue at 600 °C.

Melt flow indexes, i.e. melt volume rates (MVR) were measured using a CEAST SI-063-BS9000-SN-1-CR-10.E27 melt flow indexer. ISO1133A standard procedure was applied (190 °C and 2.16 Kg load). Samples (5 g) were dried for 2 h under reduced pressure (0.01 mbar) at 60 °C before analysis.

The moisture was determined using a Mettler Toledo Moisture Analyzer HB 43, choosing 200 °C as operating temperature. Measurements were carried out on 10 g samples.

Differential scanning calorimetry (DSC) measurements were performed on 5–10 mg samples under nitrogen atmosphere by using a Mettler Toledo 822e calorimeter. Samples were heated from 30 to 220 °C at 10 °C/min (1st heating), cooled to −80 °C at the same scan rate (1st cooling), then heated again to 220 at 10 °C/min (2nd heating). Glass transition temperatures were measured from the inflection point in the second heating thermogram. Crystallization and melting enthalpies were evaluated from the integrated areas of melting peaks. Indium and tin were used as calibration standards.

Size exclusion chromatography (SEC) analyses were performed in $CHCl_3$ (1 ml/min) at 30 °C, using a Jasco GPC setup, made of a HPLC PU2089 Plus pump equipped with two Mixed-D PLgel columns (300 × 7.5 mm), a PLgel guard column (50 × 7.5 mm), a CO 2065 Plus column oven, a RI2031 Plus refractive index detector, and a UV2077 Plus UV–visible detector. Monodisperse poly(styrene) samples (Perkin Elmer) were used as calibration standards.

Scanning electron microscopy (SEM) was performed on cryogenically broken surface sputtered with gold using a Joel JSM model T-300 microscope. Particle diameter analysis was performed using free NIH software ImageJ 1.40 g.

Fourier transform infrared spectra (FT-IR) were recorded using a Perkin Elmer Spectrum GX FT-IR spectrophotometer on cast polymer film (chloroform solution) on KBr pellets in the 400–4000 cm^{-1} range.

Polymer films (thickness 250–350 μm) were prepared by compression moulding using a Collin P200 M melt press. Crushed blend samples were heated at 200 °C between teflon sheets for 1 min, then pressure (5 MPa) was applied at 200 °C for 1 min.

Tensile tests were carried out according to ASTM D638 type MIII using a Tilnius Olsen H10 KT tensile tester. All specimens were conditioned for 72 h in the presence of saturated $Mg(NO_3)_2 \cdot 6H_2O$ water solution before analysis. The test was carried out at a crosshead (500 N) speed of 1 mm/min. Tensile strength, E-modulus, and percentage elongation were calculated from the load elongation curves obtained for 5–15 specimens for each sample.

3. Results and discussion

3.1. Evaluation of the processing conditions set of PLA and PBAT

As the first step to setup experimental conditions and to determine PLA and PBAT behaviour upon processing, we investigated the thermal stability of pristine PLA and PBAT by thermogravimetric analysis (TGA) in air and under nitrogen atmosphere. The onset decomposition temperature (T_d) was higher than 335 °C under nitrogen atmosphere for both polymer matrices, and a single decomposition process was detected. Under air flow PLA and PBAT appeared slightly less stable (lower T_d) and two degradation steps were detected, indicating that thermo-oxidative degradation pathways indeed occurred. Weight loss of the second step was found to be very low for PLA (2.5%) but significant for PBAT (14.4%). Finally, independently of the presence of nitrogen flow, both samples presented less than 1% mass residue at 600 °C. The thermal stability of the polyesters was further evaluated by isothermal TGA in air, at 150 and 200 °C for 30 min. Notably, the thermograms did not display any degradation step, and after 30 min the mass loss was evaluated as 0.5% for PBAT and 0.4% for PLA. This weight loss was consistent with the presence of residual humidity: indeed, moisture analysis reported values of 0.23% and 0.30% for PBAT and PLA, respectively.

3.1.1. Polymer processing: the effect of temperature

We firstly evaluated the thermal stability of PLA and PBAT upon processing at increasing temperature, taking into account the results of the thermal stability of pure PLA and PBAT as determined by TGA.

Crude samples of both polymers were treated in a discontinuous mixer at temperature of 150, 170, 190 and 200 °C. For both polymers, increased processing temperature yielded a lower final torque, indicating reduced viscosity of the material. In the case of PBAT, the final torque values decreased from 4.2 Nm (150 °C) to 1.5 Nm (200 °C). Conversely, the processing temperature had larger influence on the torque values of PLA, which decreased from 16 Nm to 5 Nm by increasing the temperature from 150 to 200 °C. Accordingly, MVR for PLA shifted from 4.2 cm^3/10 min (at 20 °C, pristine PLA) to 8.6 cm^3/10 min (at 190 °C), indicating that PLA undergoes thermal degradation upon processing (Fig. 1). On the other hand, MVR of PBAT slightly increased from 24.2 cm^3/10 min (at 20 °C, pristine PBAT) to 30 cm^3/10 min (at 190 °C), indicating the high thermal stability of PBAT upon processing (Fig. 1).

SEC analyses of PLA and PBAT processed samples in $CHCl_3$ were performed (Table 1). As temperature increased, PLA displayed a progressive shift of the elution peak towards lower molecular weights, broadening the distribution, consistent with a higher DI (Fig. 2). Indeed, PLA's $\overline{Mn}$ shifted from 12.0×10^4 (pellets) to 7.1×10^4 (PLA_200), and, in addition, DI values increased from 1.75 to 1.98.

Note that the distributions of the processed polymers display higher contribution from low molecular weight fractions, revealing the occurrence of chain scission. This phenomenon is confirmed by