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Characterization and ageing study of poly(lactic acid) films plasticized with oligomeric lactic acid

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ABSTRACT

Poly(lactic acid) (PLA) was melt-blended with a bio-based oligomeric lactic acid (OLA) plasticizer at different concentrations between 15 wt% and 25 wt% in order to enhance PLA ductility and to get a fully biodegradable material with potential application in films manufacturing. OLA was an efficient plasticizer for PLA, as it caused a significant decrease on glass transition temperature (T_g) while improving considerably ductile properties. Only one T_g value was observed in all cases and no apparent phase separation was detected. Films obtained by compression moulding were stored during 3 months under ambient controlled conditions and thermal, mechanical, structural and oxygen barrier properties were studied in order to evaluate the stability of the PLA–OLA films over time. Blends with 20 and 25 wt% OLA remained stable and compatible with PLA within the ageing period. Besides, PLA–20 wt% OLA formulation was the only one which maintained its amorphous state with adequate thermal, mechanical and oxygen barrier properties for flexible films manufacturing.

1. Introduction

The use of bio-based and biodegradable polymers in food packaging applications is considered a potential solution for the serious ecological problems caused by the inherent non-biodegradability of the common petrochemical-based polymers [1–3]. Poly(lactic acid) (PLA) is one of the most promising bio-based polymers for eco-friendly packaging, not only for its biodegradability and renewable source, but also for its processability, lightness and transparency [1,2].

The addition of plasticizers to PLA allows the production of flexible films by improving its inherent brittle nature [1–3]. Concerning food contact materials, plasticizers should meet several requirements, in particular being non-toxic and cited in the positive list of additives allowed to be used in contact with food [4]. They should also show good compatibility with the polymer and provide suitable thermal, mechanical and barrier properties. Besides transparency, their low volatility and low migration to foodstuff are also relevant parameters to ensure the permanence of the plasticizer in the polymer matrix, and consequently the stability of films during their shelf life [3]. Several compounds have been studied as potential PLA plasticizers, such as triacetine, citrate esters [5–9], glycerol [10], malonate oligomers, adipates and polyadipates [13,14], poly(ethylene glycol) (PEG) [8,10,15–17], poly(propylene glycol) (PPG) [18] or their copolymer PEPG [19]. However, their incorporation into PLA without showing phase separation over time was restricted to concentrations lower than 20 wt% in all cases.

Physical ageing is an inherent characteristic of the amorphous phase in polymers involving chains rearrangement, spontaneously reducing their free volume towards a thermodynamic equilibrium. This process is time and temperature dependent and leads to the decrease in the molecular mobility of the polymer chains, directly affecting the material physical and mechanical properties, such as glass transition temperature (T_g), crystallinity, brittleness and tensile strength. Such changes could induce phase separation in the system or even plasticizer exudation [5–7,17,19,20].

One approach to increase the compatibility of the additive with PLA would be adding a compound with similar intermolecular forces able to strongly interact with the polymer, preventing phase separation and reducing crystallization with a negative effect on ductility over time. Besides, if the plasticizer has relatively high molar mass, migration to foodstuff would be limited. In addition, if these additives were produced from renewable resources, a fully bio-based material could be obtained.

Oligomeric lactic acid (OLA) could be proposed as an alternative to common plasticizers for PLA by taking advantage of their similar chemical structure, relatively high molar mass and renewable

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origin [21]. Martin and Averous (2001) found that an oligomeric lactic acid was an efficient plasticizer for PLA at 20 wt% because it induced a decrease in T_g and elastic modulus of 20 °C and 63%, respectively, whereas elongation at break increased up to 200%. However, no ageing studies were performed and consequently the stability of these formulations over time cannot be ensured. Based on these preliminary results, it is expectable that higher amounts of OLA plasticizers could be successfully incorporated into PLA, obtaining even more ductile materials. However, lower T_g values could affect their morphological stability over time with a gradual loss of mechanical properties.

The aim of this work was to evaluate the effects of ageing on the structural, thermal, mechanical and oxygen barrier properties of PLA films plasticized with OLA at 15, 20 and 25 wt%, since these concentrations can be considered as those with possibilities to maximize the plasticizer effect with no phase separation. Miscibility and stability over time in PLA–OLA blends will be determined for their use in flexible food packaging.

2. Experimental

2.1. Materials

A commercial poly(lactic acid) PLA 2003D ($M_n = 98{,}000$ g mol^{-1}, $M_w/M_n = 1.85$, $T_g = 59.7$ °C, 4 wt% D-isomer) from NatureWorks LLC (Minnetonka, USA) was used as polymeric matrix. An oligomeric plasticizer based on L-lactic acid, OLA 00A/8, was synthesized and kindly supplied by Condensia Química S.A. (Barcelona, Spain) following a polymerization method already described in a patent [21]. OLA 00A/8 (named OLA for simplicity) is a slightly coloured liquid with a density of 1.10 g cm^{-3}, a glass transition temperature of −40.4 °C (determined by differential scanning calorimetry, DSC), a molar mass of 957 g mol^{-1} (M_n) and a polydispersity index of 1.4 (determined by size exclusion chromatography, SEC).

2.2. Preparation of PLA–OLA films

PLA pellets were dried over night at 60 °C under vacuum in order to avoid PLA hydrolysis during processing. To ensure a high contact area and an accurate incorporation of the plasticizer into the polymer matrix, pellets were milled to a final particle size of approximately 1 mm using a RETSCH ZM200 Ultra Centrifugal Mill (Haan, Germany). Then, PLA was manually pre-mixed with the plasticizer at 15, 20 and 25 wt%. After 1 h at room temperature, materials were melt-blended in a Haake Polylab QC, ThermoFischer Scientific (Walham, USA), equipped with a pair of high-shear roller rotors, at 50 rpm during 8 min. The temperature was set at 170 °C but it increased to 176 °C during mixing due to the mechanical shearing. Blends were then processed into 14 × 14 cm^2 films (approximately 220 μm thickness) by compression moulding at 170 °C in a Carver Inc. Hot Press (Wabash, Indiana, USA). Materials were melted by keeping them between the press plates for 5 min at atmospheric pressure. Then, pressure was gradually increased during 2 min up to 5 MPa and maintained for 5 min. Neat PLA was processed in the same way in order to get a reference material.

The obtained films were stored for three months at 25 °C ± 1 °C and 50% relative humidity (RH) in a Dycometal-CM81 climatic testing chamber (Barcelona, Spain). The evolution of structural, thermal and mechanical properties upon ageing was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray scattering (WAXS), tensile testing, scanning electron microscopy (SEM) and oxygen transmission rate (OTR).

2.3. Material characterization

2.3.1. Thermogravimetric analysis (TGA)

TGA data were obtained on a Mettler Toledo thermal analyser, model TGA/SDTA 851e (Schwarzenbach, Switzerland). Samples of approximately 7 mg were heated at 10 °C min^{-1} from room temperature to 700 °C under nitrogen atmosphere (flow rate 50 mL min^{-1}).

2.3.2. Differential scanning calorimetry (DSC)

DSC analyses were performed on a TA Instruments DSC Q2000 (New Castle, DE, USA) under a dry nitrogen gas flow rate of 50 mL min^{-1}. After different storage times, samples were sealed in aluminium pans and heated from −30 °C to 180 °C at 10 °C min^{-1} to identify possible changes in crystallization and melting transitions due to ageing. DSC analyses were followed by quenching to −30 °C and further heating to 180 °C at 10 °C min^{-1}. Glass transition temperatures (T_g) were also determined during the second heating scan for plasticized PLA formulations after processing, once the thermal history was erased in the first heating scan.

2.3.3. X-ray diffraction (XRD)

Wide-angle X-ray scattering (WAXS) of materials was performed on a Bruker D8-Advance (USA) diffractometer, equipped with a Cu K_α radiation source ($\lambda = 1.546$ Å), operating at 40 kV and 40 mA as the applied voltage and current, respectively. The incidence angle (2θ) was varied between 2° and 90° at a scanning rate of 2° min^{-1}.

2.3.4. Mechanical properties

Tensile tests were performed using a universal test machine IBERTEST ELIB 30 (Ibertest, Madrid, Spain), equipped with a 5 kN load cell. Tests were performed with rectangular probes (100 × 10 mm^2) at a crosshead speed of 10 mm min^{-1} and an initial grip separation of 50 mm. Elongation at break (ε_{tB}%) and elastic modulus (E) of films were calculated from the resulting stress–strain curves according to ASTM D882-01 standard [22]. All values reported are the average of five measurements (±standard deviation).

2.3.5. Scanning electron microscopy (SEM)

A JEOL model JSM-840 (Jeol USA Inc., Peabody, USA) scanning electron microscope, operated at 12 kV, was used to observe the surface and cross-sections of films previously sputtered with gold. Films were submerged in liquid nitrogen and fractured to expose the cross-sections for SEM studies.

2.3.6. Oxygen transmission rate (OTR)

The oxygen transmission rate (OTR) tests were carried out in an Oxygen Permeation Analyser 8500 from Systech Instruments (Metrotec S.A, Spain). Films with homogeneous thickness (225 ± 10 μm) were selected for each formulation. Circular samples (14 cm diameter) were clamped in the diffusion chamber at 25 °C. Pure oxygen (99.9%) was introduced into the upper half of the chamber while nitrogen was injected into the lower half, where an oxygen sensor was placed. The oxygen volumetric flow rate per unit area of the membrane and per time (OTR, cm^3 m^{-2} day^{-1}) was continuously monitored until a steady state was reached. The permeability coefficient (OP) is proportional to OTR*e (e = thickness, mm). Therefore, we used the OTR*e results to compare the oxygen barrier properties of the films.

3. Results and discussion

3.1. Characterization of PLA–OLA films

The thermal stability of PLA–OLA films was studied by TGA just after processing in order to analyse the effect of the plasticizer