Research article

Effect of simulated mechanical recycling processes on the structure and properties of poly(lactic acid)

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ABSTRACT

The aim of this work is to study the effects of different simulated mechanical recycling processes on the structure and properties of PLA. A commercial grade of PLA was melt compounded and compression molded, then subjected to two different recycling processes. The first recycling process consisted of an accelerated ageing and a second melt processing step, while the other recycling process included an accelerated ageing, a demanding washing process and a second melt processing step. The intrinsic viscosity measurements indicate that both recycling processes produce a degradation in PLA, which is more pronounced in the sample subjected to the washing process. DSC results suggest an increase in the mobility of the polymer chains in the recycled materials; however the degree of crystallinity of PLA seems unchanged. The optical, mechanical and gas barrier properties of PLA do not seem to be largely affected by the degradation suffered during the different recycling processes. These results suggest that, despite the degradation of PLA, the impact of the different simulated mechanical recycling processes on the final properties is limited. Thus, the potential use of recycled PLA in packaging applications is not jeopardized.

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1. Introduction

Poly(lactic acid) (PLA) is an aliphatic polyester produced, at industrial scale, by ring-opening polymerization of lactide, a cyclic oligomer of lactic acid. The lactic acid is obtained from the fermentation of glucose, derived from agricultural sources such as corn, potato or sugar beet (Reddy et al., 2013). PLA present some interesting properties, such as its biodegradability, good processability, low cost production, low environmental impact and optical and mechanical properties similar to those of polystyrene or poly(ethylene terephthalate) (PET) (Auras et al., 2010). These good properties have caused a growing interest in PLA, making it one of the most important bioplastics in the market, specifically in packaging applications, with a global production capacity of 0.21 million tons in 2016. Furthermore, it is projected a sustained growth of the production of PLA, reaching the 0.5 million tons in 2020 (Aeschelmann and Carus, 2016).

This expected growth of the production, and consumption, of PLA could lead to some social and environmental problems in coming years. Firstly, the sustenance and health of poor countries might be threatened, as farmers could exchange the cheap food production for the high value crops used in the manufacture of PLA and others biopolymers (Mülhaupt, 2013). Secondly, there is concern about the management of the wastes derived from the massive use of PLA, since the commercial grades used in packaging applications degrade at low rate in comparison with the accumulation of wastes (Niaounakis, 2013). These problems highlight the need to study the potential of extending the life of PLA based products, in order to reduce the consumption of essential raw materials and the generation of wastes.

There are several alternatives for the valorization of PLA wastes. Piemonte (2011) carried out Life Cycle Analysis for PLA, evaluating four different final scenarios: incineration, composting, anaerobic digestion and mechanical recycling. The results showed that, from an environmental point of view, the best alternative for the valorization of PLA wastes is the mechanical recycling. However, mechanical recycling presents some associated costs, which are mainly related with the logistics of the recovery and separation of the different materials. In the case of PLA this is very important, since PLA can contaminate other plastics present in the recycling

stream, such as PET, decreasing the quality of the recycled products. Therefore, it is necessary to evaluate the cost of separation of PLA, and to develop a viable recovery system for this polymer. Due to this potential costs, it is necessary to evaluate the profitability of the mechanical recycling of PLA. In this regard, Cornell reported that the critical mass for the mechanical recycling to be profitable was 200,000 tons/year (Cornell, 2007). This critical mass has been exceeded in 2014, so the mechanical recycling should be feasible from an economical point of view. Besides the profitability of the process, it is also important to study the effect of the mechanical recycling on the performance of PLA, since if there is an important decrease of the properties of the recycled materials, the mechanical recycling would not be viable, compromising the low environmental impact of PLA (Niaounakis, 2013; Soroudi and Jakubowicz, 2013).

Although the relevance of the mechanical recycling of PLA is clear, to our best knowledge, there is little reported data about the effect of different mechanical recycling process on the performance of PLA. Pillin et al. (2008) reported that after seven reprocessing cycles, a commercial grade of PLLA showed a decrease of 60% in the molecular weight, increased crystallization ability but no significant changes in the hardness and Young modulus measured by nanoindentation. Żenkiewicz et al. (2009) found in their studies with PLLA, an important decrease of the tensile strength and thermal stability after 10 reprocessing cycles. Nascimento et al. (2010) studied the effect of an extrusion process followed by an injection process in the structure and thermal and mechanical properties of PLA, concluding that a single reprocessing step does not have a significant impact on the performance of the polymer. Brüster et al. also reported a 30% reduction of the molecular weight and an increase on the crystallization ability after 3 reprocessing cycles (Brüster et al., 2016). These studies provide useful information about the effects of the thermomechanical degradation on some properties of PLA; however, they do not consider the degradation of PLA during its service life, and the potential impact it might have on the performance of the recycled polymer.

The main objective of this work is to study the effect of degradation in use and different simulated mechanical recycling processes on the structure and properties of PLA. A commercial grade of PLA, commonly used in packaging applications, was melt compounded and transformed into films. Then, two different recycling processes were studied. One process consisted of an accelerated thermal and photochemical ageing, to simulate the degradation in use, and reprocessing by extrusion and compression molding. The other recycling process included the same accelerated ageing process, but also introduced a demanding washing step prior to the reprocessing. The effect of these recycling processes was measured by means of dilute solution viscosimetry (IV), attenuated total reflectance infrared spectroscopy (FTIR-ATR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), UV–Vis spectroscopy, haze measurements, instrumented nanoindentation tests and gas permeability measurements.

2. Materials and methods

2.1. Material description and sample preparation

A commercial grade of PLA designed for packaging applications (Ingeo 2003D, Natureworks™), with a melt mass-flow rate of 6 g/10 min (2.16 kg at 210 °C) was used. Prior to processing the pellets were crystallized for 20 min at 100 °C and dried in a vacuum oven at 85 °C for 2 h. Afterwards, the samples were processed by melt compounding in a Rondol Microlab twin-screw microcompounder, with L/D = 20 and a screw speed of 60 rpm. The barrel temperature

profile from hopper to die was 125,160,190,190,180 °C.

The obtained materials were then molded by compression into films with a thickness of 230 ± 10 μm in a IQAP-LAP hot-plate press at 190 °C, beginning with a melting step, with no pressure, for 5 min, followed by a degasification step for 2 min, and finally the samples were cooled between cold plates, using a pressure of 14 MPa for 5 min.

In order to simulate the mechanical recycling of the polymer, the films of the virgin polymer were first subjected to an accelerated ageing process, which included 40 h of photochemical degradation in an Atlas UVCON chamber, equipped with eight F40UVB lamps. The samples were also exposed to thermal degradation in a convection oven at 50 °C for 468 h. A portion of these aged samples was washed at 85 °C for 15 min, in a solution of NaOH (1.0% by weight) and a surfactant (Triton X, 0.3% by weight). Finally, all aged samples were reprocessed by extrusion and compression molded into films, following the process explained above.

According to the recycling process there were three different materials: PLAV, which was not reprocessed, PLAR, which was recycled without the washing step, and PLARW which was recycled with the demanding washing step at 85 °C. Before the characterization, all the samples were subjected to physical ageing, at room temperature, for 3 weeks.

2.2. Characterization techniques

Infrared spectra of the different materials were recorded in a Nicolet iS10 spectrometer, equipped with an Attenuated Total Reflectance (ATR) accessory. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 16 scans. The FTIR spectra were corrected using the software Omnic 9.2.41, and normalized using the band at 1450 cm^{-1}, which has been reported as an internal standard (Kister et al., 1998).

The overall transmittance in the visible light region was measured according to the ISO 13468 standard, using a Shimadzu 2401 PC UV–Vis spectrophotometer equipped with a Shimadzu integrating sphere, using a scan speed of 200 nm/min. The haze of the different materials was measured according to the ISO 14782 standard, using a Minolta CMD3600D Spectrocolorimeter, with a diffuse/8° geometry. The value of the haze is given by the following expression:

$$\% \text{ Haze} = \frac{\tau_D}{\tau_T} \times 100 \tag{1}$$

where τ_D is the diffuse transmittance and τ_T is the total transmittance.

The intrinsic viscosity (IV) was measured at 25 ± 0.5 °C using an Ubbelohde viscosimeter and chloroform as solvent.

Thermogravimetric analysis of the different samples was carried out using a TA Instruments TGA2050 thermobalance. Samples of ≈ 14 mg were heated at 10 °C/min from room temperature to 800 °C in dry nitrogen (30 cm^3/min).

Differential scanning calorimetry (DSC) analysis was performed on samples of about 7 mg, in standard aluminum pans, using a Mettler–Toledo DSC 823e calorimeter, under nitrogen atmosphere. The data was recorded at a heating rate of 10 °C/min. The samples were first heated from 20 to 220 °C, and then kept at 220 °C for 3 min to erase thermal history. After that, the samples were cooled to 0 °C, and finally a second heating scan was performed until 220 °C. The crystallinity of PLA was determined by Eq. (2):

$$\chi(\%) = \frac{\Delta H_M - \Delta H_{CC}}{\Delta H_\infty} \times 100 \tag{2}$$