Effect of accelerated ageing and mechanical recycling on the structure and properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) formulations

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Introduction
The production of biobased and biodegradable polymeric materials has gained much interest in recent years, due to threatening environmental concerns caused by massive usage of conventional plastics. Among the biobased and biodegradable bioplastics, polyhydroxyalkanoates (PHAs) is a family of polyesters produced by microorganisms as energy and intracellular carbon reserve. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is one the most interesting PHAs, because of its flexibility, ductility and improved processability in comparison with poly(3-hydroxybutyrate) (PHB), the most known member of the PHAs group (Tebaldi et al., 2019).

Despite the environmental advantages of using biobased and biodegradable plastics, end-of-life scenarios still play an important role in the sustainability of these materials and their circular economy framework. Among the potential end-of-life scenarios is mechanical recycling, which would allow to reduce the emissions and the consumption of raw materials implied in the manufacture of PHBV. Consequently, the main aim of this work is to analyze the effect of accelerated ageing and melt reprocessing on the structure and properties of a commercial grade of PHBV.

Materials and methods
PHBV PH016 was kindly supplied by Ercros S.A. PH016 is PHBV grade with 1.6 % of hydroxyvalerate content. Oligomeric lactic acid (OLA) Glyplast OLA 2, a commercial plasticizer, was kindly supplied by Condensia Química S.A.

PHBV with different OLA amounts (10, 15 and 20 %wt.) were melt compounded in a Rondol Microlab twin screw extruder at 180 °C and hot pressed into films (200 ± 10 µm thickness). The resulting materials were subjected to an accelerated ageing protocol, washed, grinded and melt reprocessed in the same conditions. The samples were characterized by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), solution viscometry, Fourier transform infrared spectroscopy (FTIR), tensile tests and gas barrier properties measurements.

Results and discussion
Figure 1 shows the thermal characterization results, by means of DSC and TGA, of the pure PHBV before and after mechanical recycling (PHBV and r-PHBV, respectively).

Figure 1. DSC cooling scans (a) and TGA curves (b) of neat PHBV before and after mechanical recycling.
It can be seen on Figure 1a that mechanical recycling caused an important increase (approximately 40 °C) on crystallization temperature. This change can be related to the degradation of the polymer during recycling, since shorter polymer chains have increased mobility, which allows them to form crystalline more easily (Rivas et al., 2017, Dedieu et al., 2022). Regarding the thermal stability of mechanically recycled PHBV, it can be seen on Figure 1b that mechanical recycling led to a slight decrease of the onset decomposition temperature of the polymer. This result can also be attributed to the degradation of the material, since shorter polymer chains have lower thermal stability. However, despite the decrease on the thermal stability of the material, the onset decomposition temperature is above the processing window for PHBV.

**Conclusions**

The obtained results point out that mechanical recycling has negative effects on the thermal properties of PHBV, because of the thermal degradation of the polymer during recycling. This behavior highlights the need of developing methods to decrease the degradation during recycling or to optimize the performance of the recycled materials.

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**References**

