Solid-state polymerization on degraded PHBV: A cheap and effective alternative for biopolymer revalorization.

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Keywords: Solid-state polymerization, biodegradable polymers, circular economy, PHBV
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Introduction

The current trends in economic and demographic terms are leading to extremely high product demand and irrecoverable ecological damage. Among all the environmental impact concerning solid waste, plastic waste dumping is one of the most threatening issues that human society and ecosystems are facing up (Scalenghe, 2018). Conventional plastics are widely used in all sorts of applications due to their outstanding properties (mechanical and optical properties, chemical resistance, etc). Nevertheless, they are derived from petroleum, they are mostly not biodegradable, they are extremely durable and some of them contain toxic additives. To sort out this issue, one of the most promising alternatives is the use of biobased biodegradable polymers. Biobased, since they are derived from renewable resources, minimizing the carbon footprint. And, biodegradable, due to their ease to be assimilated by media microorganisms that convert materials into natural substances such as water, carbon dioxide or compost (Bucci et al., 2005; Maga et al., 2019).

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) is a promising biodegradable biobased polymeric candidate to substitute conventional non-biodegradable conventional polymers. PHBV belongs to the polymer group polyhydroxyalkanoates (PHAs). These polymers are produced from microbial synthesis, which involves low production and high sale prices. Consequently, PHBV production is not suitable for the extremely high demand for polymers. Despite outstanding achievements have been reached by the scientific community (Policastro et al., 2021), recycling, reusing and revalorizing of PHBV waste could make the difference. Nevertheless, biobased biodegradable polymers can suffer severe degradation in use and are susceptible to be further degraded during the mechanical recycling, thus decreasing the properties of the final product compared to the virgin one (Pfaendner, 2022).

There are several methods for improving the properties of recycled plastics: blending with virgin plastics, using fillers and additives, etc. Solid-state polymerization (SSP) is one of the most promising methods because of its simplicity, it is cost-effective and environmentally friendly alternative, as it does not require additives or solvents. SSP is a thermal process, which consists of slight heating at temperatures below its melting point in vacuum or inert atmosphere. Polycondensation occurs and the sort chains get connected forming larger chains, thus compensating for the effect of the polymer degradation (Beltrán et al., 2020). In this work it is analyzed the effect of SSP on the structure of PHBV previously subjected to severe hydrolytic degradation.

Methodology

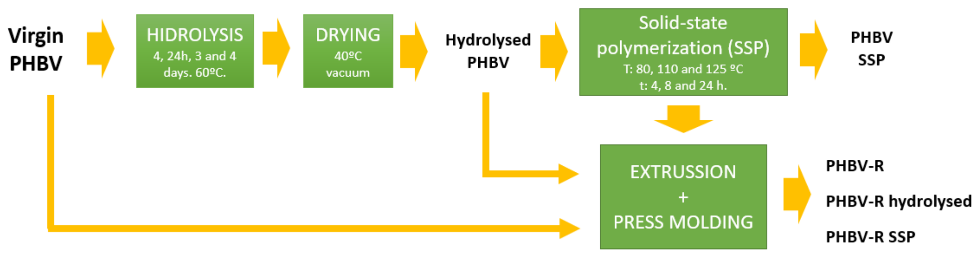

Figure 1. Scheme of the process.

The used methodology is summarized in Figure 1. Hydrolysis, solid-state polymerization (SSP) and extrusion procedures were followed taking as a reference previous tests with PLA in our research group (Beltrán et al., 2020). PHBV was degraded in water at 60 ºC for different times, then dried at 40 ºC in vacuum and finally subjected to SSP for degradation.SSP was carried out at different temperatures (80, 110 and 125 ºC) and exposure times (4, 8 and 24 h). Then the samples were extruded, and compression molded. The resulting materials were characterized by means of Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and intrinsic viscosity measurements.

Results and discussion

The results show that SSP can effectively modify the structure of degraded PHBV. As an example, Figure 2 presents the Raman spectra of the virgin (PHBV), degraded (PHBV_H) and re-graded (PHBV_SSP) samples.

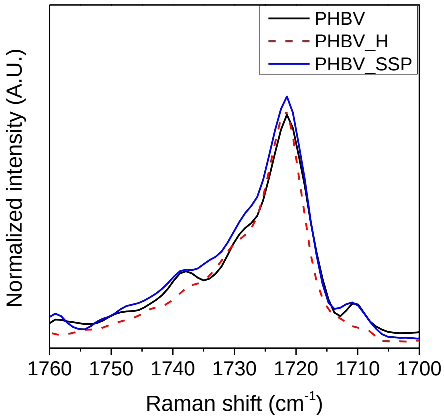

Figure 2. Raman spectra of PHBV, PHBV_H and PHBV_SSP.

The band at 1720 cm^{-1} corresponds to the C=O stretching of the ester group present in the highly ordered crystalline fraction of the polymer, while the small absorption at 1740 cm^{-1} is due to the C=O stretching in the amorphous region. PHBV_H does not show the absorption band corresponding to the amorphous region, contrary to virgin PHBV and PHBV_SSP. Additionally, the PHBV_H spectra show a slight shift to higher frequencies, which is related to the presence of acid groups and suggests the degradation of the sample (Izumi & Temperini, 2010). PHBV_SSP does not show this shift, which can be related to an increase of the molecular weight due to the polycondensation reactions. Thus, the results appear to indicate that SSP is an outstanding method to revalorize PHBV waste in a cost-effective and eco-friendly way.

Acknowledgements

Authors received funding from European Union’s Horizon 2020 research and innovation program under grant agreement No. 860407 (BIO-PLASTICS EUROPE), the UPM project RP2205430163, and ETSI Industriales project ETSII-UPM22-PU01. Authors would like to acknowledge the collaboration of Ercros S.A. for kindly supplying PHBV samples.

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