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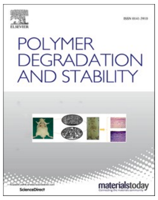

Effects of solid-state polymerization on the structure and properties of degraded poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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ABSTRACT

In the transition from a linear to a circular economy, polymer source and end-of-life scenarios must be considered when selecting a plastic for a given application. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a highly promising alternative to fossil fuel-based polymers in certain applications, because it is a biodegradable and biobased polymer with some good properties. When possible, mechanical recycling is the best option, over chemical and organic recycling, for PHBV waste. However, it must be considered that PHBV is a biopolyester that can undergo significant degradation during its use, and that degraded PHBV residues generate low-performance recycled materials, thus greatly reducing the feasibility of mechanical recycling. In this context, solid-state polymerization (SSP) is proposed as a simple, green, and cost-effective alternative to reverse the effect of the degradation and valorize the residues. In this work, PHBV residues with different levels of degradation have been obtained and subjected to SSP in vacuum for different times and temperatures, without solvents or catalysts, in order to study the effects of SSP on the structure and properties of the residues and optimize the process. The effect of SSP on the viscosity of the recycled material, obtained by melt processing the waste, has also been studied. The results indicate that the effects of the SSP depend largely on the level of degradation of the waste and that significant improvement in molecular weights and viscosities (up to 40 %), and thermal stability, can be achieved when wastes with significant degradation are treated.

1. Introduction

There is a broad consensus that bio-based polymers, such as bio-polyurethanes (bio-PU), polyhydroxyalkanoates (PHAs), poly(lactic acid) (PLA) and others, can play an important role in the transition towards a circular economy of plastics, since they come, totally or partially, from renewable sources. Due to the consumption of CO_2 in obtaining their raw materials, these plastics have a lower carbon footprint than polymers that come from oil. Moreover, several of these plastics are biodegradable enough to produce compost under industrial conditions and even in home composters.

The above social and environmental advantages explain the rapid growth in the consumption of biobased plastics. According to Skoczinski et al., while the overall market for plastics grows at 3-4 %, the compound annual growth rate for biobased polymers is as high as 8 %, and this trend is expected to continue in the coming years [1]. However, the use of biodegradable biobased plastics also presents some issues. One of the most important is the selection of the raw materials to obtain the polymers. Although several of these polymers can be obtained from agri-food residues [2], currently many of them are obtained from food raw materials such as corn or sugar cane. Therefore, excessive consumption of biobased plastics could make these raw materials more expensive, thus complicating access to food for some people [3]. This problem calls into question the real sustainability of the use of biobased plastics.

To improve the sustainability of the use of biobased plastics, it is important to analyze the possible end-of-life scenarios for their waste. The best destination, above organic and chemical recycling, is mechanical recycling [4–10] since it reduces the need for raw materials and the carbon footprint of the plastic. Waste for mechanical recycling can

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include both post-industrial and post-consumer waste. The former is in many cases a residue generated in the factory itself, which have not been seriously contaminated or degraded, so their recycling is usually carried out because it does not require complex separation or purification stages. Post-consumer waste recycling is much more complicated because waste from different plastics appears mixed and contaminated. Complex and expensive separation and purification operations are required that make this recycling unfeasible for minority plastics such as PLA or PHAs [2].

However, distributed recycling initiatives have recently been launched, which also affect biobased plastics. In the distributed recycling of plastics, a user (or group of users) locally and selectively collects a certain type of waste, carries out its mechanical recycling and uses or markets the recycled plastic obtained. As it is a selective and local collection, expensive transport, separation, and purification stages are avoided, which makes the mechanical recycling of certain minority plastics viable. An example can be the mechanical recycling of PLA used in 3D printing that can be carried out, for example, on a university campus, although the recycling of PLA for different uses is not feasible on a national scale [11–13].

Another problem with the mechanical recycling of biobased plastics is the degradation that occurs during the recycling stages, which is added to the variable degradation that occurs during the use of the plastic. This problem is especially important in biopolyesters such as PHAs or PLA that are prone to thermal and hydrolytic degradation [14–16]. Degradation processes cause a decrease in the average molecular mass that is usually accompanied by a decrease in mechanical properties and viscosity [16–18]. The drop in viscosity is very important because it complicates the processing of recycled plastic by manufacturers.

Therefore, it is important to develop procedures that make it possible to reverse the effects of degradation, that is, to regrade the plastic in such a way that properties are recovered at a level sufficient to use or commercialize the recycled plastic. For biopolyesters such as PLA or PHAs, different authors have reported the efficiency of regrading through various procedures based on the use of additives such as peroxides or chain extenders [15,19,20]. The improvement of properties of recycled plastic using clays [21] or different organic fillers [22] has also been reported.

Some of the most interesting methods for the regradation of plastics such as biopolyesters may be those based on solid state polymerization (SSP). In SSP methods, condensation polymers such as polyesters and polyamides are subjected to a thermal treatment, either in a vacuum oven or in an inert atmosphere, at temperatures below the melting point, to eliminate water and favor the displacement of the equilibrium towards the condensation and formation of new bonds [23,24]. In addition to the atmosphere, it is necessary to carefully select the temperature and the treatment time, to avoid that thermal degradation predominates over condensation. Thus, an increase in the average molecular mass can be achieved, with subsequent increases in viscosity and performance of the material. They are simple methods that do not require solvents, or melt polymer treatments, or expensive equipment. Although catalysts can be used, the SSP can also be carried out without them, thereby avoiding the presence of catalyst residues in the treated material. Furthermore, the main by-product is water, so they can be considered environmentally benign and cost-effective methods [25].

In addition to PET and PA, SSP-based methods have been employed to control the molecular weight, structure, and properties of polyesters such as PLA [26–30] and poly(buthylene succinate) [31,32]. In PHAs the use of SSP has been studied to a much lesser extent. Regarding its use in polymer recycling, SSP-based methods may be especially suitable because they allow the recovery of molecular weight and viscosity in residues that have suffered degradation during use. SSP is used for this purpose in polymers such as PET [25] and its use has also been proposed to regrade PLA waste and improve the performance of the recycled material [11,33]. In this way it is possible to valorize plastic waste in processes that can be addressed by any recycler.

In this work, the application of SSP to the recovery of degraded residues of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has been studied. PHBV is a highly promising biobased polymer, with some properties comparable to isotactic polypropylene [34], which belongs to the polyhydroxyalkanoates (PHAs) group. PHAs are fully biodegradable thermoplastic polymers produced by certain microorganisms as a carbon and energy storage system [2,35,36]. The chemical composition of the polymer depends on the microorganism and the carbon source used to feed it. PHBV has aroused special interest in recent years due to some good properties, like those of conventional polymers such as polypropylene [1,37–39]. The presence of two different acids as monomers makes PHBV less brittle than other PHAs that are homopolymers, such as poly(hydroxybutyrate).

Currently, the main destinations for PHBV post-consumer waste are incineration and landfill [40]. Taking into account that issues such as the rational use of raw materials, and the carbon footprint of plastic, would improve significantly if the waste were recycled, in recent years different authors have studied the mechanical recycling of PHBV [9,10,16,40–43]. In all cases, the results have confirmed the feasibility of the mechanical recycling.

However, it is necessary to remember that PHBV is susceptible to hydrolytic degradation and has low thermal stability, so the postconsumer waste of this plastic can show low average molecular mass and viscosity values. SSP-based methods can be very useful to treat PHBV waste and obtain better performing recycled plastics. Considering that the effectiveness of these methods for upgrading the waste depends to a large extent on factors such as the level of degradation of the residue, which alters the concentration of end groups, and the time and temperature of the thermal treatment, the main objective of this work has been to study the effect of those factors on the structure and some properties of the PHBV waste. The effect of SSP on the intrinsic viscosity after melt processing the waste was also evaluated. No solvents or catalysts were used in order to reduce the environmental impact of the SSP.

PHBV samples were subjected to hydrolytic degradation at 60 °C for different periods of time, to obtain materials with different degradation levels. The degraded materials were subjected to different SSP processes and, subsequently, some of them were processed by extrusion and compression molding. All materials were characterized by thermal analysis, infrared spectroscopy, microhardness, and intrinsic viscosity measurements. Changes in the surface were studied by contact angle measurements. Molecular weight distributions (MWD) were obtained by gel permeation chromatography. The results indicate that, depending on the starting degradation level of the residues, significant improvements in PHBV residues can be obtained in a simple and environmentally acceptable way using solid-state polymerization.

2. Experimental section

2.1. Materials

Commercial grade PHBV, (PH016), with 1.6 % of hydroxyvalerate (PH016), was kindly supplied by Ercros S.A. (Spain). More than 99 wt. % of the material is of biological origin. The melt flow rate is MFR = 5–10 g/10 min, measured at 190 °C and 2.16 kg, following the standard ISO 1133–2, and the melting temperature is 170–176 °C.

2.2. Sample preparation

Hygrothermal degradation of virgin unprocessed PHBV in powder form was carried out at 60 °C in distilled water for 4, 24, 72 and 96 h. After degradation, the samples were dried at 40 °C in vacuum to constant weight. Solid-state polymerization (SSP) was carried out (on the materials also in powder form) for different times (4, 8, and 24 h) at different temperatures (80, 110 and 125 °C), in a vacuum oven (100 mbar). Samples of virgin, degraded, and thermal treated PHBV were processed in a counter-rotating twin-screw extruder (Rondol Microlab Twin Screw microcompounder, France, $L/D = 20$), with and a screw speed of 60 rpm and the following temperature profile, from hopper to die: 125, 160, 185, 185, 180 °C. The compression molding was performed at 180 °C to obtain films with a thickness of 200 ± 20 µm in an IQAP LAP hydraulic press (IQAP, Barcelona, Spain). Fig. 1 and Table 1 shows the schematic representation of the process and the description and code names of the tested, respectively.

2.3. Characterization

To evaluate the effect of the hygrothermal degradation on the structure of PHBV, as well as the effectiveness of the different SSP treatments to reverse the effects of the degradation, the structure and properties of the materials were characterized by means of intrinsic viscosity (IV) measurements, gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), contact angle measurements, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Vickers microhardness tests. FTIR, UV–Vis, thermal analysis, microhardness and contact angle measurements were carried out on samples in the form of sheets obtained by compression moulding.

GPC was used to test the changes in the molecular weight distribution (MWD). The chromatographic system supplied by Waters consists of a refraction index detector and two Styragel packed Waters columns (HR 1 and HR 4, 7.8 × 300 mm). Chloroform stabilized with amylene (99.9 %, ACROS Organics) was used as mobile phase, with a flow rate of 1 mL/min at 35 °C. Polystyrene standards were used for the calibration. Three solutions of each material were prepared and tested. Average molecular weights (M_n and M_w) and polydispersities are shown in Table S-1. The intrinsic viscosity was tested following the standard ISO 1628–1:2021, using an Ubbelohde viscometer with chloroform as solvent, at 25 ± 0.5 °C. Three solutions (of 6, 5.3 and 4.7 mg/mL) of each material were used. The standard deviation values are shown in the corresponding figures and the relative standard deviation (RSD) values were equal to or less than 10 %.

As for the FTIR, a Nicolet iS10 spectrometer was used, equipped with a diamond Attenuated Total Reflectance (ATR) accessory. The spectra (16 scans at a resolution of 4 cm^{-1}) were normalized using the 1452 cm^{-1} band as internal reference. This band, assigned to a bending mode in $–CH_3$ groups, has been reported to be a suitable internal standard for PHBV [44] and PLA [45].

UV–Vis transmittance spectra were recorded in a Cary 1E UV–Vis spectrophotometer at a scanning speed of 400 nm/min. The overall light transmission in the visible region (400–800 nm) was calculated from the normalized spectra, according to the ISO 13468 standard, by using air as 100 % reference.

The Vickers hardness of the samples was measured using a Type M Shimadzu microhardness tester. A load of 300 g was applied during 10 s using a Vickers pyramidal indenter. Each measurement was repeated six times. RSD values were less than 1.4 %.

Contact angle was measured in films of the samples using a Theta Lite Attention Tensiometer (Biolin Scientific, Gothenburg, Sweden) and the software program "One Attention". The static water contact angle (ϴ) formed by a single droplet onto the material was measured at least five times on dry samples using a 4 µL sessile drop of deionized water as test fluid at room temperature, and the average values are reported. RSD values were less than 8 %. Images were recorded every 10 s.

Table 1
Summary and description of all samples.

Sample	Description
PHBV	Virgin
PHBV_H4h	Hydrolyzed 4 h
PHBV_H1d	Hydrolyzed 1 day
PHBV_H3d	Hydrolyzed 3 days
PHBV_H4d	Hydrolyzed 4 days
PHBV_H1d_SSP4h110C	Hydrolyzed 1 day, SSP 4 h at 110 °C
PHBV_H1d_SSP8h110C	Hydrolyzed 1 day, SSP 8 h at 110 °C
PHBV_H1d_SSP24h110C	Hydrolyzed 1 day, SSP 24 h at 110 °C
PHBV_H3d_SSP4h110C	Hydrolyzed 3 day, SSP 4 h at 110 °C
PHBV_H3d_SSP8h110C	Hydrolyzed 3 day, SSP 8 h at 110 °C
PHBV_H3d_SSP24h110C	Hydrolyzed 3 day, SSP 24 h at 110 °C
PHBV_H3d_SSP8h80C	Hydrolyzed 3 day, SSP 8 h at 80 °C
PHBV_H3d_SSP8h125C	Hydrolyzed 3 day, SSP 8 h at 125 °C
PHBV_H4d_SSP8h110C	Hydrolyzed 4 day, SSP 8 h at 110 °C
PHBV_R	Virgin, after reprocessing
PHBV_H3d_R	Hydrolyzed 3 days, after reprocessing
PHBV_H3d_SSP8h110C_R	Hydrolyzed 3 day, SSP 8 h at 110 °C, after reprocessing

Thermogravimetric analysis was performed in a TA Instruments TGA2050 thermobalance with samples of ~12 mg, using 30 mL/min of dry nitrogen, between 40–800 °C at 10 K/min. The thermal transitions of the samples were evaluated using DSC tests, which were performed in a TA Instruments DSC-Q20 calorimeter whit a dry nitrogen flow of 50 mL/min and samples of ~5 mg in standard aluminum pans. The temperatures and heating/cooling rates were: first heating (30 to 200 °C) at 5 K/min, constant temperature (200 °C) for 3 min, cooling (200 to 0 °C) at −5 K/min, constant temperature (0 °C) for 3 min, second heating (0 to 200 °C) at 5 K/min. The crystallinity, X_C (%), of PHBV was determined by Eq. (1).

$$X_C = \frac{\Delta H_m}{\Delta H_0} \cdot 100 \tag{1}$$

where ΔH_m (J/g) is the enthalpy of the melting transition and ΔH_0 (J/g) is the melting enthalpy of a 100 % crystalline PHBV sample, 109 *J/g* [46]. Taking into account that crystallinity can also be calculated from the heat evolved during melt crystallization, the melt crystallization enthalpy (ΔH_c, J/g) values were also determined.

3. Results and discussion

Like all biopolyesters, PHBV is sensitive to thermal and hydrolytic degradation [47,48]. Therefore, PHBV can suffer severe degradation during its service life, especially at high temperatures in applications in close contact with water. In hydrolytic degradation, chain scission reactions take place preferentially at the ends of the chains in a reversible process that is autocatalyzed by carboxylic acid end groups [47]. This

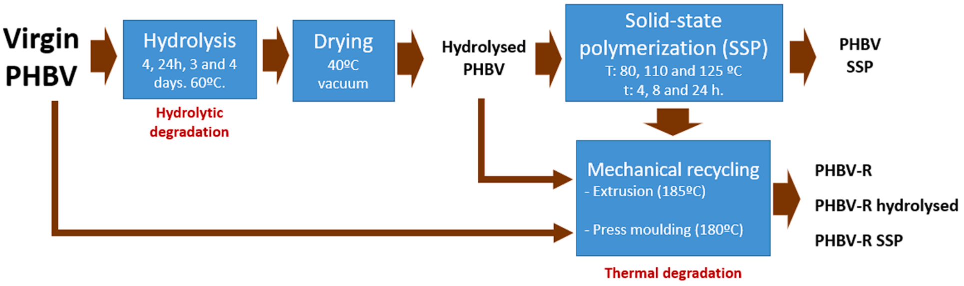

Fig. 1. Scheme of the process.

degradation in use is important because it shifts the MWD towards lower molecular weights, lowering the averages and increasing the concentration of very low molecular weight tails. The presence of degraded waste is very negative for the mechanical recycling of plastic. In addition to leading to low molecular weight recycled materials, the degraded residues show low viscosity, which complicates the melt processing of the material. In addition, the presence of low molecular weight tails, with high mobility, favors degradation during mechanical reprocessing inside the extruder, at high temperatures (above 180 °C) and shear stresses, thus leading to recycled materials with lower mechanical performance.

On the other hand, PHBV (and the other PHAs) suffer significant thermal degradation at high temperatures, such as those used in the melt compounding, even in absence of water. This thermal degradation, which has been widely studied, causes random chain scission via cis-elimination reactions (McLafferty rearrangement) to form shorter polymer chains with carboxylic acid end groups and olefinic acids, such as crotonic acid and 2-pentenoic acid [48,49]. Fig. 2 shows schemes of the hydrolytic and thermal degradation processes. It is important to note that hydrolytic degradation is reversible in theory, when working under the right conditions.

The main goal of this work is to study the feasibility of using SSP to reverse the pernicious effects of degradation in residues, that is, this work intends to study the effect of thermal treatments on the structure and properties of PHBV residues, and the materials obtained from them by mechanical recycling. To do this, firstly, PHBV samples with different levels of degradation have been obtained by hygrothermal degradation at 60 °C in water for different periods of time. Subsequently, different thermal treatments have been applied in vacuum, varying time and temperature, to force condensation and determine the optimal conditions for the SSP of this material.

3.1. Effects of hygrothermal degradation and thermal treatments on the structure of PHBV

Firstly, the degradation of PHBV during the hygrothermal treatments has been evaluated by means of intrinsic viscosity (IV) measurements. Fig. 3 reveals the effect of the treatment in water at 60 °C on the intrinsic viscosity of PHBV.

Fig. 3 shows that there is significant hygrothermal degradation under these conditions. PHBV loses half of its initial IV value after 3 days of treatment and two thirds after 4 days of degradation. The degradation kinetics can be described through eq. (2).

$$Ln(IV_t) = Ln(IV_0) - 0.252(\pm 0.01) \cdot t(R^2 = 0.9942) \quad (2)$$

where IV_t is the intrinsic viscosity (mL/g) at time t, IV_0 is the viscosity of the virgin polymer, t is the time (d) and 0.252 is the rate constant (d^{-1}) in this case. This result is in good agreement with those obtained by other authors in the study of the hydrolytic degradation of PHBV [50], and PLA [27]. These authors observed that the logarithm of the average molecular weight decreases linearly as the hydrolysis time increases, thus revealing a characteristic behavior of autocatalytic degradation processes, in which the -COOH end groups formed in the hydrolysis catalyze the following hydrolysis [51]. The autocatalytic nature of the hydrolysis of PHBV has been also observed in PHBV reinforced with wollastonite [52].

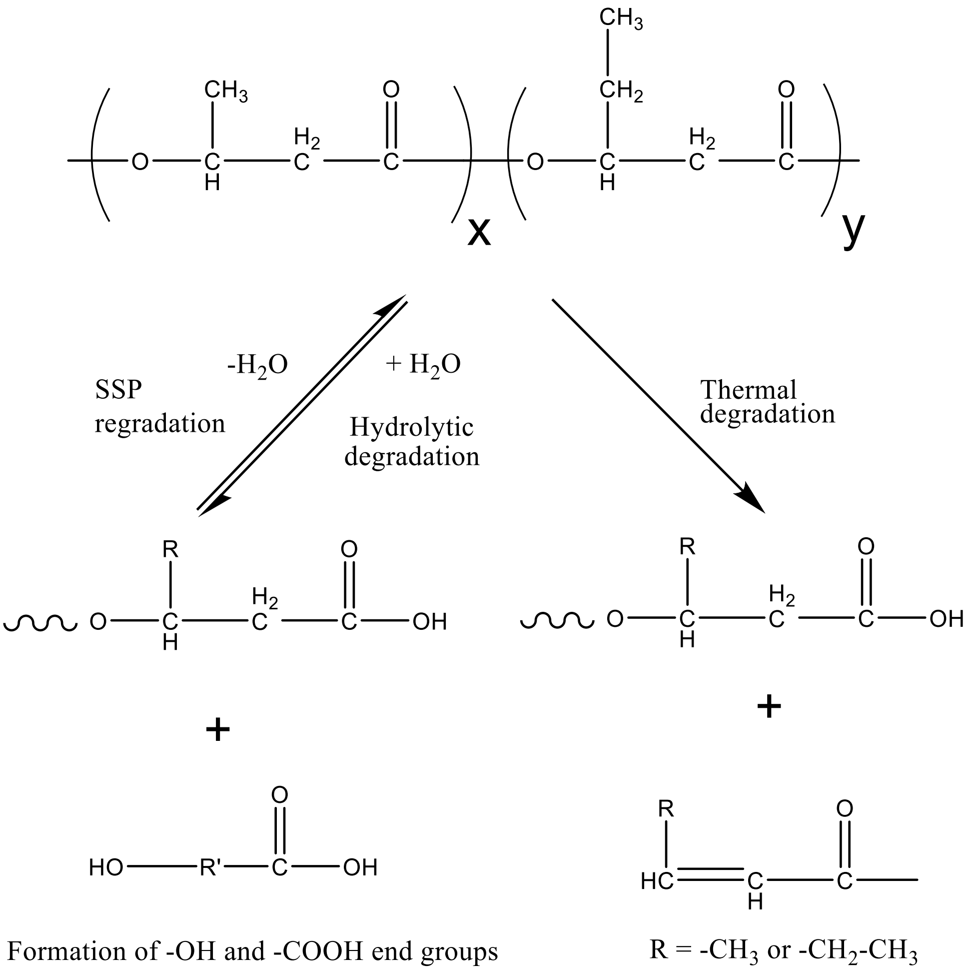

Fig. 2. Chemical structure of PHBV and degradation processes.

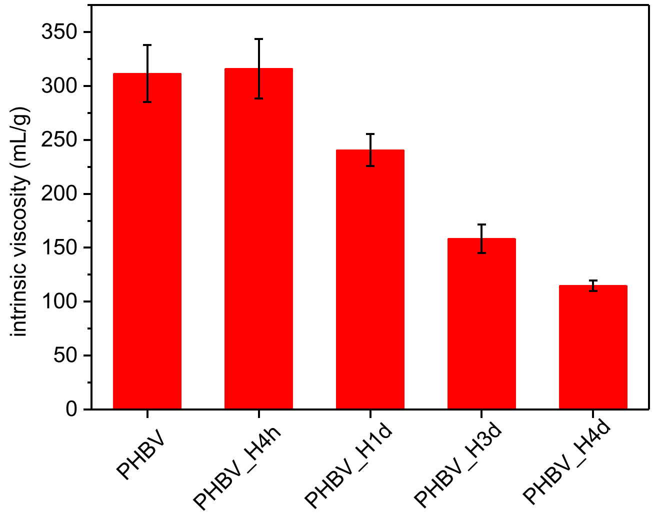

Fig. 3. Intrinsic viscosity values of degraded PHBV.

Although the degradation process will be analyzed later using IR spectroscopy, the possible degradation pathways are those shown in Fig. 2. It can be thought, a priori, that hydrolytic degradation is more important than thermal degradation, both at 60 °C in water as well as during the service life of the material. This is important because hydrolytic degradation is a reversible process, so the decrease in IV can be attempted to be reversed by SSP treatments under appropriate conditions. These conditions have been studied in polymers such as PET [23,25,53] and PLA [27,30,33], but we do not know this information in the case of PHBV. Therefore, the SSP of PHBV has been studied using thermal treatments in vacuum at different temperatures. Taking into account that the efficiency of the SSP can be expected to depend on the initial degradation level, because this level determines the concentration of reactive groups for condensation, the study has been carried out in samples with different hygrothermal degradation times.

The effects of SSP at 110 °C on the IV of samples subjected to different hygrothermal degradation are shown in Fig. 4. Both for highly degraded samples, with 3 days of degradation, and for less degraded samples, with only 1 day of degradation, SSP at 110 °C makes it possible to partially reverse the effect of degradation and recover part of the lost IV. However, the effect of the SSP is much more important in the strongly degraded sample; while in the sample degraded for 1 day the increase in IV is 6.7 %, in the sample subjected to hygrothermal degradation for 3 days an increase as high as 58 % can be obtained. The SSP in highly degraded samples is so effective that, after 8 h of thermal treatment, the IV of the highly degraded sample practically equals that of the slightly degraded sample. All these results can be explained considering that SSP facilitates a condensation process opposite to hydrolytic degradation (see Fig. 1), and that both the initial concentration of reactive groups for condensation and the chain mobility, which are higher in the most degraded sample, play a main role in the SSP process.

The results also indicate that the efficiency of the SSP depends on the time of the thermal treatment time. In the two cases presented in Fig. 4, it can be observed that a maximum appears in the IV at an intermediate treatment time, which is close to 8 h. This maximum can be explained as the result of two opposing effects; as SSP time increases, water removal increases, thus favoring condensation, which increases average molecular mass and IV, but also increases thermal degradation, leading to chain scission and decreased IV. A similar result has been reported for another biopolyesters such as PLA [27,33].

Fig. 5 shows that the efficiency of the SSP also depends on the temperature of the thermal treatment. Considering the previous results (Fig. 4), a severely degraded sample (3 days) and the treatment for 8 h were selected for these tests. The temperatures tested were 80, 110 and 125 °C, all of them below the melting point. Although the differences observed between the tested temperatures are so small that they fall within the confidence intervals, a tendency to define an optimal temperature does seem to be observed, since the result at 110 °C is better than those obtained at 80 and 125 °C. As with the thermal treatment times, the existence of an optimal temperature for the SSP could be justified as the result of two opposing effects. On the one hand, a low temperature would be ineffective because the chain mobility would be too low; on the other hand, a too high temperature could lead to unacceptable thermal degradation with chain scission.

The above results show that thermal treatments can reverse, at least partially, the IV loss observed in degraded PHBV. This fact can have an important application in the mechanical recycling of PHBV, since the existing degradation in the PHBV residues that are going to be recycled can play a very pernicious role during their mechanical reprocessing. The presence in the degraded residues of -OH and -COOH groups, as well as short chains with high mobility, facilitates the degradation of the polymer during extrusion at high temperatures, so that the elimination of these functional groups and short chains in waste, prior to extrusion, can lead to less degradation during mechanical reprocessing and therefore better properties of the recycled material.

To study the effects of degradation and thermal treatments on the IV

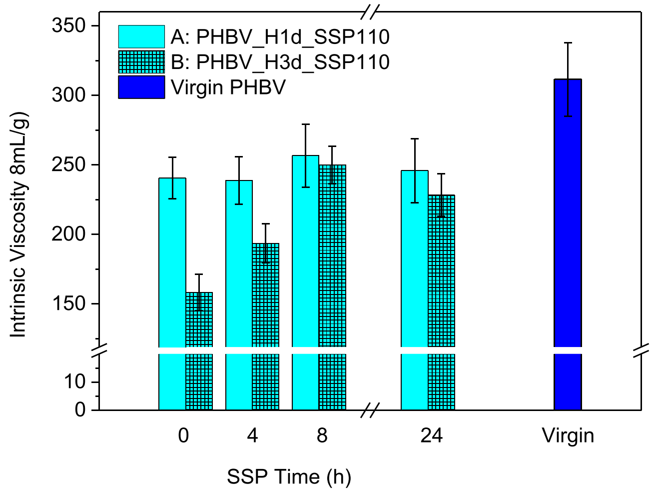

Fig. 4. Changes in the intrinsic viscosity induced by SSP at 110 °C: A) PHBV degraded for 1 day; B) PHBV degraded for 3 days. IV of virgin PHBV is also included for comparison.

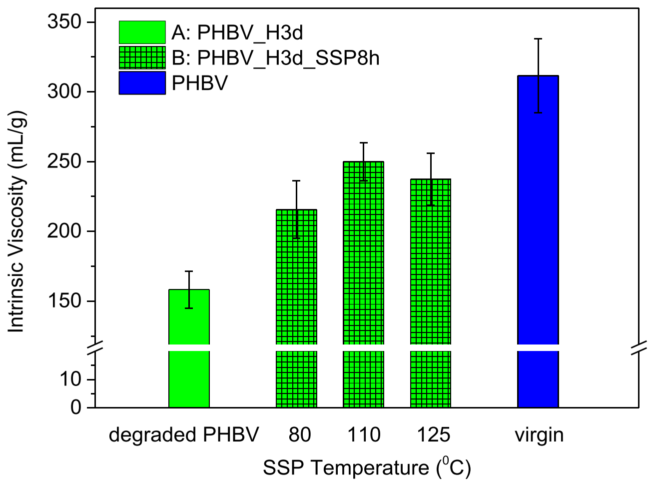

Fig. 5. Changes in the intrinsic viscosity induced by 8 h of SSP at different temperatures: (A) PHBV degraded for 3 days; (B) PHBV degraded for 3 days subjected to SSP. The IV value of virgin PHBV is also included for comparison.

of the recycled polymers, different samples of the virgin polymer, the degraded polymer, and the same polymer degraded and subjected to SSP treatment, were extruded and compression molded, after which IV values were measured.

The results, which are shown in Fig. 6, firstly reveal that the virgin polymer undergoes significant degradation during processing by extrusion and compression, since the IV drops by almost half (from 311.6 to 166 mL/g). The polymer degraded for 3 days, PHBV_H3d, shows an even lower viscosity after recycling, specifically 101 mL/g, which confirms the hypothesis that the degradation of the residues is very pernicious during recycling as it generates significant additional degradation. However, the thermal treatment of the degraded waste during 8 h at 110 °C, in vacuum, allows reaching an IV value of 140 ml/g, which means an increase of 37.5 % over the IV of the degraded and recycled waste. It should be noted that this value, 140 mL/g, is similar to the IV of the virgin polymer after reprocessing, 166 mL/g, that is, the heat treatment makes it possible to greatly reduce the pernicious effect that the degradation of the residues has on the viscosity of the recycled polymer. Thus, these results suggest that SSP treatments could very positively contribute to the technical feasibility of mechanical PHBV recycling.

The set of changes observed in the IV of PHBV, both during the degradation processes and in the thermal treatments, can be explained if we accept that the main process during the degradation at 60 °C is the hydrolytic chain scission, which reduces the IV of the polymer, and that thermal treatments cause an SSP that partially reverses the results of the degradation. However, the possible existence of another thermal degradation process that generates unsaturated compounds, especially during heat treatments for SSP, remains to be studied. To evaluate this question, as well as the validity of the proposed hypothesis, the changes in the structure and chemical composition of the different materials have been analyzed using IR spectroscopy and size exclusion chromatography.

Fig. 7 allows us to compare the representative GPC curves of the virgin polymer, the same polymer subjected to severe degradation for 4 days, and the degraded polymer subjected to a thermal treatment for 8 h at 110 °C under vacuum, which allow analyzing the changes in the molecular weight distribution (MWD). The values of the average molecular weights, referred to polystyrene standards, as well as the polydispersity, are shown in Table S-1. The material subjected to severe degradation shows a remarkable shift of the MWD curve towards lower molecular weights, which confirms that an important chain scission process takes place. The average molecular weight decreases accordingly, passing the mass average (Mw) from 400 KDa for the virgin polymer to 153 KDa for the degraded one (Table S-1). This scission process could explain the significant decreases in IV shown in Fig. 3.

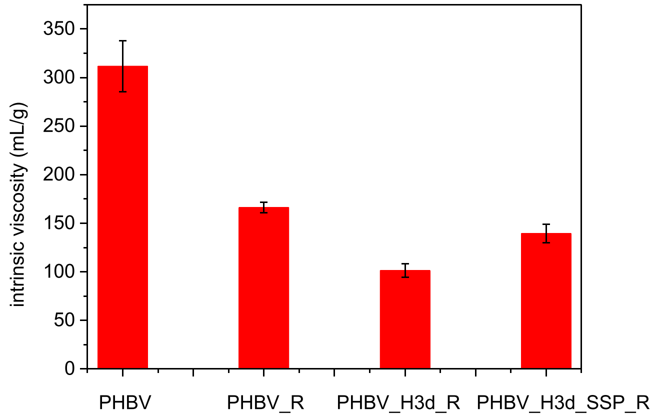

Fig. 6. Effects of the degradation (3 days) and SSP (8 h at 110 °C) on the intrinsic viscosity of reprocessed PHBV. The IV value of virgin PHBV is also included for comparison.

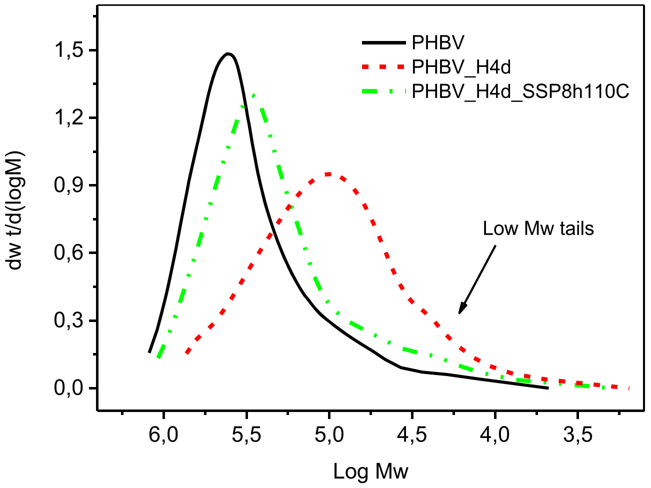

Fig. 7. MWD curves corresponding to virgin PHBV, PHBV degraded for 4 days (PHBV_H4d), and the degraded polymer treated for 8 h at 110 °C under vacuum.

Fig. 7 also shows that hygrothermal degradation causes a noticeable increase in the relative amount of low molecular weight fragments (indicated in the figure), which are barely observed in the trace of the virgin polymer. This increase is important because these low molecular weight molecules are characterized by their high mobility and reactivity, which makes them highly effective for polymer degradation during mechanical recycling.

Regarding the effects of thermal treatments, both Table S-1 and Fig. 7 reveal that some of the effects of degradation can be largely reversed when the treatment is carried out under the appropriate conditions. As a consequence of the treatment, the MWD curve shifts towards higher molecular weights and the Mw value reaches 301 KDa; i.e., although the initial value of 400 KDa was not recovered, the thermal treatment allowed the Mw value of the degraded polymer to be doubled. These results can be explained by the hypothesis proposed, considering that the thermal treatment causes an SSP, shifting the equilibrium shown in Fig. 2 towards the formation of longer chains through condensation reactions.

To finish the study of the changes in the MWD curves, it is worth mentioning that polydispersity slightly increases in the degradation process from 2.6 ± 0.4 to 3.0 ± 0.3 (4 days), as expected in a chain scission process (Table S-1). The thermal treatment does not cause a decrease (polydispersity = 3.3 ± 0.1), thus indicating that, in addition to polycondensation, the treatment also causes chain breakage, which is reasonable considering that the SSP is carried out at high temperatures. A similar result was observed in the study of the SSP of PLA [33], which confirms the importance of properly selecting the conditions of the SSP so as not to cause excessive degradation. However, although the heat treatment causes chain breakage, Fig. 7 shows that a net disappearance of low molecular weight tails is achieved, which could explain the positive effect of SSP treatments on the mechanical recycling of the polymer, which has been shown in the Fig. 6. The elimination of short reactive chains in the degraded waste during thermal treatment prevents these chains from catalyzing the degradation of the polymer during the melt reprocessing stage.

Changes in the chemical nature of the polymer have been studied using FTIR-ATR spectroscopy. Fig. S-1 shows a representative spectrum of the materials subjected to degradation, as well as the spectrum of the degraded material subjected to a thermal treatment for 8 h at 110 °C and allows comparison of these spectra with that of the virgin polymer. It should be noted that the presence of characteristic bands of C=C bonds has not been observed, neither in the degraded polymer nor in the material regraded by the thermal treatment. The absence of characteristic bands of C=C bonds indicates that the thermal degradation process shown in Fig. 2, which leads to the formation of unsaturated compounds such as crotonic acid, does not play an important role in this case, not even in the processes that take place during heat treatments. This result is reasonable if we take into account that these thermal degradation processes in PHBV are important only at high temperatures, equal to or higher than those used in melt processing [48,49] and that these temperatures are much higher than those used in our treatments.

The main changes that take place in the IR spectrum as a consequence of the degradation and thermal treatments can be observed in detail in Fig. 8, which shows the stretching vibrations zone of C=O groups. It is known that these C=O vibrations are sensitive to the physical-chemical environment. For example, it is possible to distinguish the absorption corresponding to C=O groups of ester groups in amorphous environments, which shows a maximum near 1740 cm^{-1}, from the absorption corresponding to C=O groups in crystalline domains, which appears at a lower wavenumber and energy (about 1720 cm^{-1}) due to the stronger interactions that C=O groups present in crystalline environments [54,55]. Furthermore, absorption may also appear at lower energies if the C=O groups present hydrogen bonds. The stretching vibrations of the C=O groups present in carboxyl groups appear at shorter wavelengths, around 1700 cm^{-1}.

It can be seen in Fig. 8 that the degradation of the polymer causes the appearance of additional absorption in the zone 1690 - 1720 cm^{-1}, which can be assigned to the appearance of new carboxyl groups in the degradation process, and the establishment of new hydrogen bonds between those carboxyl groups and the ester groups of the polymer. In this way, the IR spectra confirm the existence of hydrolysis in the ester groups of the polymer, in good agreement with the IV and GPC results. The appearance of absorption around 1700 cm^{-1} causes a slight displacement of the maximum towards lower energies, from 1720.5 to 1719.1 cm^{-1}. However, the spectrum corresponding to the polymer regraded by the thermal treatment is much more similar to the spectrum of the virgin polymer. It is observed that some absorption disappears in the 1690–1720 zone, which allows the absorption maximum to appear at almost the same wavenumber as in virgin plastic. Fig. S-2 shows the same behavior in samples degraded for four days. These results can be explained because of the polycondensation processes that take place during the thermal treatment.

Thus, the analysis of the infrared spectra confirms the proposed hypotheses; thermal degradation does not play a relevant role in the conditions used in this study and the main processes are those of the equilibrium between hydrolytic degradation that generates -COOH end groups and hydrogen bonds, and the polycondensation processes that eliminate these groups. Thermal treatments under the right conditions allow a solid-state polymerization that partially reverses the degradation results, which helps explain the positive effects observed on intrinsic viscosity, MWD curves, and on the mechanical recycling of PHBV.

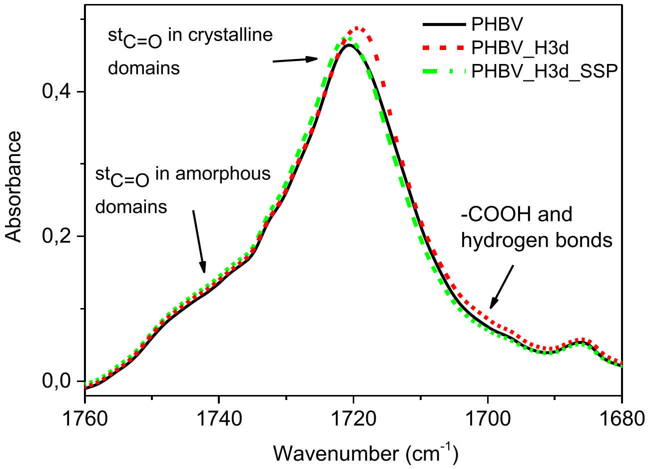

Fig. 8. IR absorption in the C=O stretching region corresponding to virgin PHBV, PHBV degraded for 3 days (PHBV_H3d), and the degraded polymer treated for 8 h at 110 °C.

3.2. *Effects of degradation and thermal treatments on the properties of PHBV*

The changes in the structure that have been discussed in the previous section translate into some changes in the properties of the final material, in addition to the changes in processing properties such as intrinsic viscosity, which have already been discussed. In this section, we discuss the changes caused by degradation and thermal treatments in thermal properties, microhardness, optical clarity, and contact angle.

Light transmission is an important optical property in materials that can be used in food packaging. In Table 2, which shows the light transmission values in the visible region of the spectrum, between 400 and 800 nm, it can be seen that the transmission decreases slightly due to the degradation process and is recovered during the thermal treatment to force the SSP. In any case, the small differences observed indicate that there are no substantial changes in the structure of the material in these processes, and that the material subjected to SSP could be used in the same applications as the virgin material. Figure S-3 shows that neither the degradation process nor the subsequent thermal treatment generates new absorption bands in the polymer that could reveal the presence of substances other than those that can be expected according to the results of Section 3.1. The small differences observed in overall transmission can be related to slight changes in light scattering due to changes in the material structure.

The changes in microhardness shown in Table 2 are so small that the differences are within the confidence intervals. This result, which has been previously observed in the SSP of PLA [33], may be due to the existence of different structural changes that cause opposing effects on the Vickers hardness. The degradation reduces the average size of the chains, as shown in Fig. 7, which results in a deterioration of the mechanical properties; however, the same degradation generates polar end groups that strengthen the interactions between chains and thus improve the mechanical properties, in a way that practically offsets the negative effect. Nevertheless, it should be noted that, although the differences are small, the material shows a slightly higher microhardness after being subjected to SSP, which may be due to the increase in the average molecular weight.

Table 2 also shows the changes in contact angle values (measured with high purity water) caused by degradation and subsequent thermal treatment. The contact angle is highly related to the surface energy that determines properties such as adhesion and wettability, which are very important in polymer films, especially in fundamental applications such as food packaging [56,57]. PHBV, as many biopolyesters, has a hydrophobic character, but degradation could change the surface polarity, thus altering its adhesion and wettability behavior. As can be seen in Table 3, the value of the angle decreases because of the degradation, going from 81.0 to 72.7° after degradation for 3 days, thus showing an increase in the water wettability and, hence, in the polymer hydrophilicity. A similar result was observed by Antunes et al. during the accelerated weathering of PHBV [55]. However, the thermal treatment

Table 2
Optical, mechanical, and contact angle properties of virgin and treated samples.

Sample	Light transmission (%)	Vickers hardness (MPa)	Static contact angle
PHBV	67.5 ± 0.3	3399 ± 35	81.0 ± 6.5
PHBV_H3d	66.3 ± 0.3	3365 ± 38	72,7 ± 2.7
PHBV_H3d_SSP8h110C	68.0 ± 0.3	3388 ± 48	84,3 ± 5.4

Table 3

DSC (cooling and second heating) and TGA results of PHBV and PHBV degraded for three days. T_c is the maximum of the crystallization peak, T_{m1} is the maximum of the first melting transition, T_{m2} is the maximum of the second melting transition, ΔH_c is the measured melt crystallization enthalpy, ΔH_m is the measured melting enthalpy, X_C is the crystallinity, T_5 is the temperature at which 5 % of the mass has been lost and T_{max} is the temperature of maximum weight loss rate.

Sample	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_C (%)	T_5 (°C)	T_{max} (°C)
PHBV	65.0	167.3	174.5	71.3	86.2	79	272.3	296.4
PHBV_H3d	84.9	167.3	175.1	84.5	89.0	82	267.1	293.6
PHBV_H3d_SSP8h110C	84.7	167.4	175.1	79.8	84.7	78	272.1	297.1

increases the value of the contact angle, reaching a value very similar to that of the virgin polymer.

These results are fully consistent with the changes in the structure and chemical composition which have been discussed in the previous section. In the degraded materials the hydrolysis creates surface hydrophilic groups, such as the -COOH groups that have been observed in the IR spectra, which explain the decrease of the contact angle with water. However, in materials subjected to thermal treatment, a clear increase in hydrophobicity is observed because the polycondensation reactions eliminate polar groups.

The effects of degradation and thermal treatment on the thermal properties of the material were studied by DSC and TGA. In the DSC analysis, each material was subjected to a first heating process up to 200 °C, above the melting point, to erase the thermal history of the material, followed by cooling to 0 °C and a second heating up to 200 °C. Fig. 9a and b show the DSC curves corresponding to the cooling and the second heating, respectively, for the virgin polymer, the one subjected to three days of degradation and the degraded one subjected to thermal treatment. The numerical values of the main thermal transitions are shown in Table 3.

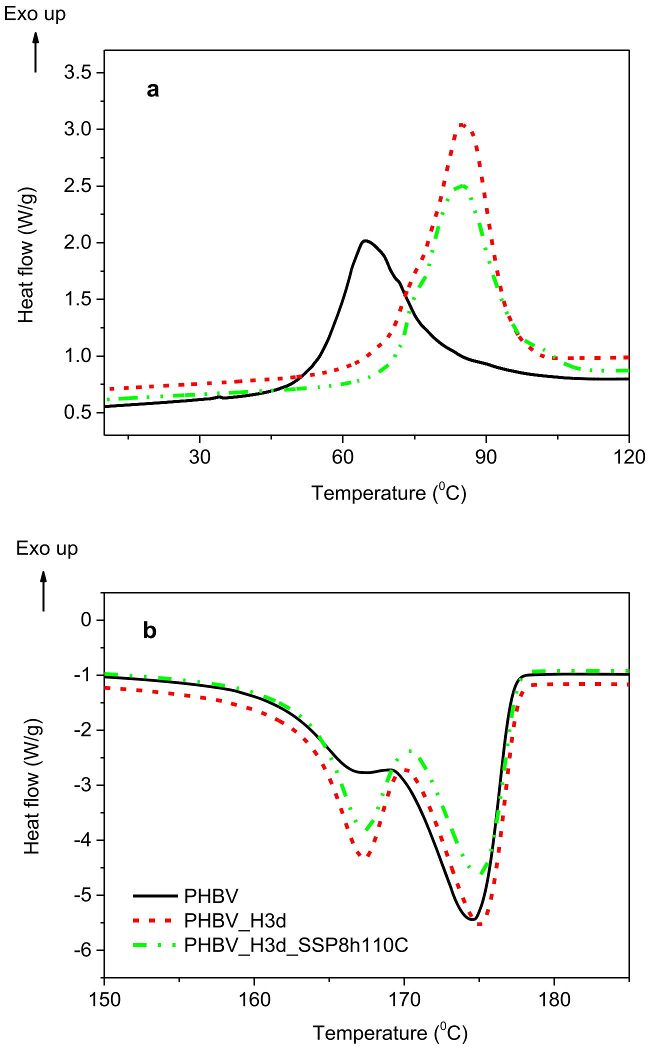

Fig. 9. Cooling (a) and second heating (b) DSC curves corresponding to virgin PHBV (solid line), PHBV degraded for 3 days (PHBV_H3d) (short dash), and the degraded polymer treated for 8 h at 110 °C under vacuum.

Fig. 9a shows that degradation has an important effect on crystallization when the polymer is cooled from the melt. The crystallization temperature, T_c, is clearly higher in the degraded material, thus revealing an easier crystallization, which can be explained as a result of the changes in the polymer structure that have been discussed in the previous section. The IR and GPC results show that the hygrothermal degradation has two consequences that can have opposite effects on polymer crystallization. On the one hand, degradation increases the concentration of -OH and -COOH end groups that can establish strong interactions, thus reducing the mobility of the chains, which can hinder the crystallization of the polymer. On the other hand, degradation reduces the average molecular weight, which can increase the mobility of the chains, thus favoring crystallization [41]. In our case this second effect is more important, which justifies the increase in T_c. It must be considered that the virgin PHBV that we have studied has a high average molecular weight, which difficult the crystallization because of the size of the chains and the high viscosity, so that the decrease in the molecular weight has a pronounced effect favoring the crystallization when the polymer is cooled from the melt.

The thermal treatment does not produce significant changes in the crystallization peak although, as shown in the previous section, it causes polycondensation processes that reduce the number of polar end groups and increase the average molecular weight. This result can perhaps be explained taking into account that the average molecular weight remains lower than that of virgin polymer even after thermal treatment and that the polydispersity is clearly higher, as shown in table S1, which could facilitate the formation of different crystalline structures with different melt stability.

This increase in polydispersity could also explain some changes observed in the polymer melting process (Fig. 9b). The PHBV studied presents a double melting peak between 160 and 180 °C, which indicates the existence of different crystalline structures with different melt stability [58]. The double peak appears due to a sequential process that includes the fusion of low stability structures, rearrangement into more stable crystalline structures and final fusion of these new structures. The hydrolytic degradation of the polymer causes a notable increase in the relative importance of the first melting peak, which may be due to the formation of shorter chains with greater polydispersity, which may facilitate the formation of crystalline structures of low melt stability. The thermal treatment does not reduce the relative importance of the first melting peak because the polydispersity is even greater than that of the virgin polymer.

Table 3 shows that degradation and heat treatment do not significantly modify the melting temperatures, which is important for the melt processing of the material. Regarding the crystallinity (X_C) determined by DSC, a slight increase is observed in the degraded material, which is explained by the greater ease of crystallization in this material. It must be taken into account that, in this method, the quality of the different crystalline structures is not considered to determine the percentage of crystallinity. The thermal treatment reduces the percentage of crystallinity to reach a value close to that of the virgin polymer. The crystallinity values shown in Table 3 were determined from the melting enthalpies, using Eq. (1). However, it is possible to also determine them from the melt crystallization enthalpies, ΔH_c, which are also shown in Table 3. The variation of ΔH_c during degradation and thermal treatments shows the same trend as the variation of ΔH_m, which confirms the validity of the results.

The effects of degradation and SSP on the thermal stability of the polymer have been studied using TGA. As can be seen in Fig. S4 and Table 3, hydrolytic degradation causes a decrease in the thermal stability of the material. T_5, the temperature at which 5 % of the initial mass has been lost, which is frequently considered an indicator of the initial temperature of thermal decomposition, drops by 5 °C due to the degradation, while the temperature of maximum mass loss rate, T_{max}, drops almost 3 °C. Although these decreases are moderate, they can play an important role in the mechanical recycling of PHBV, specifically in the use of degraded waste, since it is known that one of the limitations of this polymer is its low thermal stability. Regarding the thermal treatment, the results show that it increases the thermal stability of the material, making the TGA and DTG curves, as well as the values of T_5 and T_{max}, very similar to those of virgin material, that is, completely reversing the effect of the degradation.

The changes in thermal stability can be explained as a consequence of the differences observed in the structure of the material. Once again, it must be considered that hydrolytic degradation leads to two opposing effects on thermal stability, since the decrease in molecular weight weakens interactions between chains and reduces thermal stability, while the appearance of polar end groups allows stronger interactions to be established and increases stability. In our case, the first effect is predominant in degradation and explains the decrease in thermal stability. Thermal treatment increases stability because polycondensation reactions allow the average molecular weight to be raised. Although the molecular weight after treatment is still lower than that of the virgin polymer, the presence of some polar end groups can also contribute to increasing the stability.

The positive effect of thermal treatment on the polymer stability confirms the usefulness of SSP to recover structure and properties in degraded PHBV samples. The above results have also shown the positive effect of SSP on the recycled material. Taking into account that waste degradation is one of the main obstacles to the viability of mechanical recycling, the results obtained in this work indicate that SSP can contribute significantly to reducing this degradation and making mechanical recycling viable. Considering also that this method does not use solvents or catalysts, that the working temperature is moderate, and that the necessary equipment is simple, it can be stated that methods based on SSP are simple, green, and cost-effective alternatives to promote the recycling of PHBV.

4. Conclusions

PHBV samples were subjected to different hygrothermal degradation processes to obtain samples with different levels of degradation. Subsequently, the degraded samples were subjected to thermal treatments, without catalysts or solvents, and the changes in the structure and material properties were analyzed. Some degraded and treated materials were finally mechanically recycled. The objective was twofold: to understand the processes that take place and to evaluate the technical feasibility of solid-state polymerization (SSP) based on thermal treatments to valorize degraded PHBV waste through mechanical recycling.

Degradation causes chain scission that leads to a noticeable decrease in intrinsic viscosity and average molecular weight, an increase in polydispersity, and to the formation of low molecular weight tails and -COOH end groups. These structural changes explain a slight increase in the hydrophilicity of the surface, the increase in the crystallization temperature when the polymer is cooled from the melt, the formation of crystals of lower melt stability, and slight decreases in the thermal stability and hardness of the polymer. The thermal treatments force polycondensation, which allows the effects of degradation to be reversed, thus recovering to a large extent the structure and properties of the virgin material. The usefulness of SSP in PHBV depends strongly on the level of degradation of the residue, being more effective when the level of degradation is high. Optimal values of time and temperature of the heat treatment have been determined; if the temperature is low, the mobility of the chains and molecular segments is not sufficient, while if the temperature or treatment time is excessively high, thermal degradation limits the positive effects of SSP.

The results of this work show that degraded PHBV waste can be recovered through thermal treatments that allow effective SSP under simple, economical, and environmentally friendly conditions, since no solvents or catalysts are used. In this way, SSP methods can contribute to valorize waste and improve mechanical recycling of PHBV.

CRediT authorship contribution statement

I. Bernabé Vírseda: Data curation, Formal analysis, Investigation, Resources, Validation, Writing – original draft. **F.R. Beltrán:** Data curation, Formal analysis, Investigation, Validation. **M.U. de la Orden:** Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Writing – original draft. **J. Martínez Urreaga:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110630.

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