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Recycled Poly(hydroxybutyrate-co-valerate) as Food Packaging: Effect of Multiple Melt Processing on Packaging Performance and Food Contact Suitability

Isabelle Dedieu¹ · Chahinez Aouf¹ · Sebastien Gaucel¹ · Stéphane Peyron²

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Abstract

This study examines the opportunity of using recycled poly(hydroxybutyrate-co-valerate) (PHBV) as food packaging. The recyclability was evaluated by assessing the effect of repeated polymer processing (up to four extrusion cycles) on the structural and barrier properties of the material, as well as its ability to produce neo-formed chemicals susceptible to migrate into food. It was shown that increasing the number of processing cycles results in a decrease of the polymer molecular weight, leading to a decrease of mechanical properties, balanced by a maintenance of the crystalline structure and of the thermal stability. The oxygen and water vapour transfer properties were also maintained after four cycles suggesting that r-PHBV-based packaging can retain its property and use panel. The specific migration of crotonic acid, one of the main products of the thermomechanical degradation of the PHBV was measured in three different food simulants. In all cases, it did not exceed the specific migration limit (SML) set at 0.05 mg/Kg food, revealing the food contact suitability of non-contaminated recycled PHBV under test conditions.

Keywords Bioplastics · Polyhydroxybutyrate-co-valerate · Mechanical recycling · Food packaging · Suitability

Introduction

Plastic, with its unique set of properties (versatile, flexible, strong, cheap...) has become one of the most popular material since the second half of the 20th century. At the same time, this success is turning into an environmental and health disaster due to the plastic waste accumulation and the widespread diffusion of persistent plastic fine particles, even in living organisms [1]. Packaging is the largest end-use market segment, accounting for over 40% of total plastic usage [2]. These fossil-based materials are in ever-increasing demand due to their desirable thermomechanical and barrier properties, yet they are beyond the world's capacity to handle. In 2019, 17.8 Mt of food and drink packaging were collected in Europe, with 18.5% landfilled, 39.5% incinerated and 42% down-cycled [3]. Landfill and incineration are still

mainly used despite the Circular Economy Package adopted in 2017 by the European commission, which promotes a circular economy for plastics. In the frame of waste hierarchy, prevention should be considered as first priority, followed by preparing for re-use, materials recovery (mechanical and chemical recycling) and organic recycling. Energy recovery and disposal should be the last options envisaged [4]. Therefore, there is a gap between the current plastic waste management and the circular economy principles. This gap is even greater for alternative plastics, namely biobased and biodegradable plastics. These emerging plastics such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and polybutylene succinate (PBS) are increasingly entering the food packaging market thanks, in particular, to their deployment by major agri-business groups through a wide range of applications [5]. However, post-consumer biodegradable packaging are mainly directed towards the energy recovery lines (i.e. incineration) and are not recovered in an industrial composting facilities, as they cannot be assimilated to bio-waste of natural origin according to many national standards. Yet, biobased and biodegradable plastics are likely to follow the different end-of-life options and should be incorporated in a hierarchal end-of-life system that prioritizes material

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recycling, leading to a recovery of economic value. LCA studies and techno-economic sustainability analysis (TESA) which are based on the assessment of mechanical recyclability, economic viability, common environmental/techno-economic sustainability criteria, confirm that the organic recycling of biodegradable and bio-based plastics should be only considered when mechanical and chemical recycling are not possible [6–10]. The mechanical recycling process consists in reprocessing the polymer waste, *via* a step of reshaping in the molten state, most often by extrusion. In the case of materials intended to food contact applications, specific requirements should be respected in order to ensure the safety of the recycled material. In EU, EFSA published in 2011, the criteria to be used to ensure the safety of food contact recycled PET, involving an additional decontamination step consisting in cleaning and heat treatment. This decontamination step should be extrapolated to all other recycled plastics intended for food contact applications [11].

From a technical point of view, several investigations have addressed the mechanical recyclability of some biobased and/or biodegradable plastics. These studies, mainly focused on thermomechanical reprocessing of PLA, concluded that the thermal and mechanical properties are altered beyond a certain number of cycles [12, 13]. Only Briassoulis et al. have employed Techno-economic sustainability analyses (TESA) to address the feasibility of recycling food packaging biomaterials in a closed-loop system [9]. Among the promising biopolymers, polyhydroxyalkanoates (PHAs) have received particular attention thanks to their biocompatibility and biodegradability under natural conditions [14, 15]. Recent studies (from 2010 to 2020) on the biodegradation of PHAs in soil and marine environments were compiled in the review by Meereboer et al. The authors showed that depending on the nature of the soil and the temperature and moisture conditions, PHAs can reach up to 80% degradation in 80 to 100 days [16]. This family of bio-polyesters of microbial origin contains several homo- and copolymers with varying thermal and mechanical characteristics. Polyhydroxybutyrate-co-valerate (PHBV) is one of these copolymers, which has a great potential. During the biotechnological production, feeding and nutrient ratios may impact the valerate content which can vary from 0 to 24% inducing a modulation of the mechanical properties and flexibility of the copolymer [17]. Overall, PHBV has mechanical properties close to polypropylene and polystyrene (in terms of strength and elasticity but not flexibility), barrier properties close to those of PET, and its compliance with food contact material regulations, make it a good candidate to replace conventional plastics in the rigid food packaging category [15, 18, 19].

Although PHBV is biodegradable, this end-of-life option does not necessarily have to be favoured and can fully co-exist with possible material recycling which allows a

reduction of production costs and saving raw materials and carbon.

When considering the closed-loop mechanical recycling of PHBV for food contact applications. Two questions arise (1) how many processing cycles can PHBV withstand without losing its mechanical and barrier properties, and without producing any neo-formed chemicals (NIAS) that could migrate into food, inducing toxicity to the consumer. (2) is the mechanical recycling process capable of removing post-consumer contaminants due to previous packaging use or misuse, to comply with recycled packaging safety regulation. The second question involving the assessment of the decontamination efficiency through a challenge test will be the subject of a future work.

This study will focus on the effect of the multiple processing cycles on the evolution of the PHBV functional properties, as well as the formation of neo-formed chemicals.

Only very few studies investigated the modification of PHBV properties after reprocessing. Indeed, five cycles of extrusion followed by injection moulding at 170 °C [20] resulted in the maintenance of PHBV properties, except for a slight decrease in the fifth cycle. However, six cycles of extrusion at 180 °C led to thermal degradation of the polymer, reflected in a decrease in the molecular weight of PHBV and an increase in its crystallinity rate [21]. In the absence of a specific recommendation, PHBV-based materials are approved for food contact provided that the level of migration of crotonic acid, the main thermal degradation product of PHBV, does not exceed the permitted limit of 0.05 mg/kg food (CE/10/2011) [22].

The purpose of the present work is to investigate the functional properties of PHBV after several recycling loops, as well as the potential occurrence of crotonic acid at concentrations that may exceeds the recommended threshold. The integrated approach implemented in this study consists of monitoring the evolution of the structural characteristics of PHBV-based material (crystallinity rate and molecular weight of the polymer chains) in relation to the functional properties of the packaging (barrier and mechanical properties) throughout the reprocessing cycles and establishing an initial opinion on the opportunity of applying mechanical recycling in compliance with safety recommendations.

Experimental

Materials

PHBV with 3 mol% of 3-hydroxyvalerate (HV) was purchased from Nature plast (France). It corresponds to the PHI003 commercial grade, a pure un compounded powder produced from pure culture. According to the manufacturer, PHBV has the following properties: density = 1,25 g cm⁻³,

$T_m = 170\text{--}176\text{ }^\circ\text{C}$. Molecular weight of PHBV powder was measured and $M_w > 1,100,000\text{ g/mol}$. Boron nitride 98% was purchased from Merck. Crotonic acid (98%), ethanol (96%), acetic acid (>99%) and poly(2,6-diphenyl-p-phenylene oxide) under the trade name of Tenax (60/80 mesh) were supplied from Sigma-Aldrich.

Reprocessing Cycles

PHBV powder was mixed with 0.5 wt% of Boron Nitride as a nucleating agent. To improve the mechanical properties of polymers, nucleating agents are often used, such as Hyperform HPN-20E used for HDPE, to reduce cycle time and improve blow moulding performance [23]. Then, the mixture was dried at $60\text{ }^\circ\text{C}$ for 24 h prior to extrusion. Extrusion was carried out in a parallel twin screw microcompounder Process 11 (Thermoscientific), at 150 rpm with a uniform processing temperature of $180\text{ }^\circ\text{C}$ from the feeding to the die. The residence time of PHBV in the extruder did not exceed 3 min. Four processing cycles were performed in order to simulate the mechanical recycling. After each cycle, the granulating process was carried out at room temperature and the granulated product was dried at $60\text{ }^\circ\text{C}$ for 24 h. PHBV films with an average thickness of $300\text{ }\mu\text{m}$ were produced by thermocompression using a heated hydraulic press (20T, Pinette Emidecau Industries). About 6 g of pellets from each processing cycle were placed in a mould between two Teflon sheets and pressed with heating plates stabilized at $180\text{ }^\circ\text{C}$. The pressure was first set at 5 bars for 1 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30 s. The resulting films were finally air cooled at room temperature.

After thermocompression of the PHBV films and before any characterization of the material, all samples were conditioned at a temperature of $25\text{ }^\circ\text{C}$ and under an atmosphere with a relative humidity of 50% during 2 weeks in order to allow the secondary crystallization of PHBV [24].

Characterization Methods

Size Extrusion Chromatography (SEC)

SEC was used to determine the evolution of PHBV molecular weight throughout the reprocessing cycles. Samples were placed in sealed tubes and dissolved in a 95/5 Hexafluoro-2-propanol/Chloroform mixture at a concentration of 1 mg/mL^{-1} . Gel permeation chromatography (GPC) measurements were performed by a HP 1100 Series equipped with a PL gel $5\text{ }\mu\text{m}$ Minimixed-C column. The instrument, provided with a refractive index and UV detectors, worked using chloroform as eluent. The calibration of the instrument was constructed with polystyrene standards. The sample analyses

were performed in triplicates. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were obtained from the SEC analysis and the polydispersity index (PDI) was calculated as M_w/M_n , using the software Excel 2016.

Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a TA Instruments (Q200 modulated DSC, TA Instruments) calorimeter under a nitrogen atmosphere with a flow rate of 50 mL min^{-1} and a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Around 8 mg of sample was used for each analysis and all experiments were done in duplicate. The samples were subjected to the following thermal schedule. First heating from -30 to $200\text{ }^\circ\text{C}$, with stabilization for 3 min; then cooling down up to $-30\text{ }^\circ\text{C}$ with again a stabilization for 3 min; followed by a second heating scan up to $200\text{ }^\circ\text{C}$.

The melt crystallization temperature (T_c) was determined from the cooling scan whereas the melting temperature (T_m) and the melting enthalpy (ΔH_m) were obtained from the second heating scan after erasing the thermal history. Overall theoretical degree of crystallinity (X_c) was calculated from the melting enthalpy according to the following equation:

$$X_c (\%) = \frac{\Delta H_m}{\Delta H^\circ(\text{PHBV})}$$

where ΔH° is the melting enthalpy of 100% crystalline PHBV, i.e. 109 J/g [25].

Thermal Gravimetric Analysis (TGA)

TGA was carried out using a Mettler apparatus (TGA2) equipped with a XP5U balance (precision of 0.0001 mg). Around 8 mg of sample were heated at $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$ under nitrogen flow of 50 mL min^{-1} . Three replicates were scanned for each sample. Mass loss and first derivative of mass loss were recorded as a function of temperature, and the maximum degradation temperature (T_{deg}), corresponding to the temperature at which the degradation rate was maximum was measured.

Mechanical Properties

ISO $\frac{1}{2}$ samples were cut from the films obtained by thermocompression. Tensile properties of samples were measured using a tensile tester (Zwick BZ2.5/TN1S) with a cross-head speed of 1 mm min^{-1} . Young's modulus, elongation at break as well as tensile strength were calculated from strain-stress curves with the Matlab program, taking into account an effective cross section of 22 mm . Ten replicates were scanned for each reprocessing cycle.

Transfer Properties

The Oxygen permeability (PO_2) of the reprocessed films was determined in triplicate at 23 °C and 50% relative humidity, using an O_2 permeation chamber equipped with an integrated PSt6-type sensor (PreSens Precision Sensing GmbH). This system consists of two chambers separated by a grid where the film is placed with an open testing area of $1,26 \cdot 10^{-3} \text{ m}^2$. After applying nitrogen flesh on both sides of the film to remove the surrounding oxygen, the lower chamber was exposed to an oxygen flow of 50 mL min^{-1} , while the upper chamber was hermetically closed. By permeation, the O_2 molecules could pass through the film where the sensor stood. The system measured oxygen ingress in % for 5 days. PO_2 ($\text{mol m/m}^2 \text{ s Pa}$) was calculated according to the following equation :

$$PO_2 = \frac{J x e}{A x \Delta P}$$

where J (mol s^{-1}) is the flux of gas passing through the film, e is the film thickness (m), A , the permeation area (m^2) and ΔP , the differential partial pressure of the permeant gas across the film (Pa).

The water vapour permeability (P_{wv}) of films was determined according to a modified ASTM procedure (ASTM E96 – Standard test methods for water vapour transmission of materials). Analyses were conducted at 23 °C and a relative humidity gradient of 0 to 100% with five replicates per sample. Film samples, with $9,08 \text{ cm}^2$ area were hermetically sealed in 50 mL glass permeation cells containing 40 mL of distilled water, and were placed in a desiccator containing silica gel, for 10 days. P_{wv} ($\text{mol m/m}^2 \text{ s Pa}$) was calculated according to the following equation :

$$P_{wv} = \frac{J x e}{A x \Delta P}$$

where J (mol s^{-1}) is the flux of water vapour passing through the film, e is the film thickness (m), A , the permeation area (m^2) and ΔP , the differential water vapour pressure between the cell and the desiccator (Pa).

Migration Tests

In order to evaluate the suitability for food contact of reprocessed PHBV, crotonic acid migration was assessed in three different food simulants following the recommendation of European regulation EU 10/2011 on plastic materials and articles intended to come into contact with food [22]. These are, 95% Ethanol to simulate fatty food, 3% acetic acid to simulate acidic food and Tenax as solid

dry food simulant. The migration level of crotonic acid was measured by desorption tests. According to European standard EN 10/2011, films disks of 2.8 cm diameter were immersed in 95% ethanol or 3% acetic acid, with a surface/volume ratio of $6 \text{ dm}^2 \text{ L}^{-1}$. In the case of Tenax, a film of $3 \times 2 \text{ cm}$ was placed into Petri dish and completely covered by the simulant (0.24 g corresponding to 4 g dm^{-1}). All samples were stored at 40 °C for 10 days under magnetic stirring for liquid simulants.

Crotonic acid was quantified in each food simulant after 10 days of contact by means of UPLC-DAD analysis. For detection purposes, Ethanol 95% samples were concentrated 67 times. A standard addition procedure was applied to acetic acid 3% samples, since it cannot be easily evaporated. Tenax samples were submitted to an extraction with 5 ml methanol, during 4 days at 40 °C and under magnetic stirring. The extracts were subsequently concentrated five times. All the samples were then, injected in Acquity UPLC (Waters, Milford, MA) liquid chromatography system, equipped with a photodiode array detector (DAD). The Waters column was $100 \text{ mm} \times 2.1 \text{ mm}$, HSS T3, particles size was $1.8 \mu\text{m}$. The solvent used were A (99. % H_2O and 0.1% HCOOH v/v) and B (80% CH_3CN ; 19% H_2O ; 0.1% HCOOH) with a flow rate of 0.55 mL min^{-1} . The injection volume was $2 \mu\text{L}$ and DAD was set at 210 nm in order to detect and quantify crotonic acid which was used as external standard.

Statistical Analysis

Statistical analyses and data visualization were performed in XLSTAT (Addinsoft, 2019). The variables were checked for normality (Shapiro-Wilk test). The significance of results was examined by one-way analysis of variance (ANOVA) followed by a Tukey test with a confidence interval of 95%. Then, the significant difference between the data had been defined.

Results and Discussion

Structural Properties

The evolution of the molecular weight (M_w), polydispersity and crystallinity parameters of PHBV during the processing cycles is shown in Table 1. Cycle 0 corresponds to the first extrusion cycle transforming PHBV powder into pellets.

As M_w of PHBV commercial powder is $> 1,100,000 \text{ g/mol}$, it is worth to note that the first extrusion cycle (corresponding to cycle 0) induced the most dramatic degradation of the polymer, decreasing its molecular weight by almost 25%. Subsequently, PHBV M_w decreased with the number of processing cycles. At the end of the fourth cycle, PHBV

Table 1 Molecular weight and crystallinity parameters of PHBV films after the reprocessing cycles. Values represented are mean \pm standard deviation

PHBV	Mw (g/mol)	PDI	Tc (°C)	Tm (°C)	Xc (%)	Tdeg (°C)
Cycle 0	827,206 ^a \pm 21,831	3.8 ^a \pm 0.4	125.3 ^a \pm 0.2	177.6 ^a \pm 0.4	87.7 ^a \pm 0.7	300.2 ^a \pm 0.9
Cycle 1	815,486 ^a \pm 29,939	3.7 ^a \pm 0.1	126.1 ^{ab} \pm 0.1	177.7 ^a \pm 1.0	88.1 ^a \pm 0.6	299.4 ^a \pm 2.4
Cycle 2	683,572 ^b \pm 20,411	3.6 ^a \pm 0.3	126.3 ^{ab} \pm 0.5	177.7 ^a \pm 1.0	88.0 ^a \pm 0.4	300.8 ^a \pm 0.6
Cycle 3	662,609 ^b \pm 36,669	3.4 ^a \pm 0.4	126.6 ^b \pm 0.4	177.8 ^a \pm 0.9	89.2 ^a \pm 0.6	302.0 ^a \pm 1.2
Cycle 4	627,822 ^b \pm 15,349	3.3 ^a \pm 0.4	127.1 ^b \pm 0.1	177.3 ^a \pm 0.8	89.4 ^a \pm 0.4	299.3 ^a \pm 0.1

The letters a and b symbolize groups of significantly different values

polymer lost \sim 25% of its M_w . As previously described, the high temperatures and the shear stress that polymer undergone during the reprocessing result in a progressive chain scission, mainly attributed to the beta-elimination mechanism [26, 27]. The constant value of the polydispersity index (PDI) of the polymer observed over the five extrusion cycles supports the hypothesis of the random nature of the chain scission reactions in the polymer. The crystallinity parameters i.e. crystallization temperature (T_c), melting temperature (T_m) and crystallization rate (X_c) were respectively determined from cooling and second heating scans of PHBV films (visible in supporting data, Fig. S1). The crystallization rate of the polymer did not significantly evolve throughout the processing cycles. However, a slight increase in the crystallization temperature T_c was observed from the third cycle, indicating that the crystallization is occurring more easily when the number of cycles increases. An easier crystallization process is likely due to the reorientation of the polymer fragments after the chains scission [28, 29]. On the other hand, the crystallization rate as well as the melting temperature remained constant over the five processing cycles. Zembouai et al. [21] have observed an increase in crystallinity rate after processing PHBV with 3 wt% valerate content over six cycles of extrusion, while Zaverl et al. [20] described an opposite behaviour in the case of the copolymer exhibiting a valerate percentage of 14%, under similar processing conditions. Since these two studies also simulated the PHBV reprocessing via a polymer extrusion process, the crystallinity evolution is then likely due to the valerate content, in the absence of any nucleating agent. In our case, the use of boron nitride seems to govern the nucleation process, causing slight evolution in crystallization rate, T_m and T_c , despite the significant degradation of polymer chains. The melting temperature (T_m) remained almost constant, meaning that the fusion of crystalline fraction takes place in the same way over the reprocessing cycles. Polymer degradation should decrease the spherulites size, but the nucleation seems to be not affected by the polymer degradation in the presence of the nucleating agent [30]. This was confirmed by the constant shape of the unimodal melting peak indicating a relative stability of the distribution of the crystallite sizes [30]. The constant melting temperature at around 177 °C implies

that the process temperature scale can be kept the same at 180 °C during the five cycles. Since the polymer degradation might be enhanced when its processing occurs higher from its melting temperature, the previously observed differences in polymer degradation cannot therefore be explained by differences in the melting temperature during the process [30].

The thermal gravimetric analysis (TGA) showed almost the same degradation maximum temperatures for samples of different reprocessing cycles with no significant change has been detected over the reprocessing cycles (visible in supporting data, Fig. S2). Previous studies reported the same trend in PHA or PLA reprocessing [20, 31]. This may be explained by the relative stability of the crystallinity degree [32].

These results showed that despite a significant decrease in the polymer molecular weight, the crystalline behaviour and the thermal stability have evolved very slightly over the processing cycle. This observation is consistent with studies focusing on the impact of reprocessing on the thermal behaviour of PHA [20, 21]. However, in the context of food packaging applications, functional properties (mechanical and barrier) as well as the safety of the reprocessed materials should be taken into account in order to ensure compliance with quality requirements and regulation.

Mechanical Properties

Figure 1 shows pictures of the film samples obtained over successive cycles and reveals that the reprocessed materials do not present any obvious visual changes. The macroscopic optical properties such as colour, opacity and smooth texture do not appear to be altered by the reprocessing.

The mechanical properties of the material reflect its ability to provide a high-performance packaging for food and define which types of packaging (bottles, trays, flexible bags, etc.) can be produced. Based on these tensile tests, the evolution of the mechanical properties of the materials over the processing cycles are summarized in Table 2, and the tensile stress vs. strain curves are shown in supporting data, Fig. S3.

These values confirm that PHBV can be considered as a brittle and stiff material, which exhibits low ductility due to its high crystallinity. Compared to other semi-crystalline

Fig. 1 PHBV films over four extrusion-compression cycles

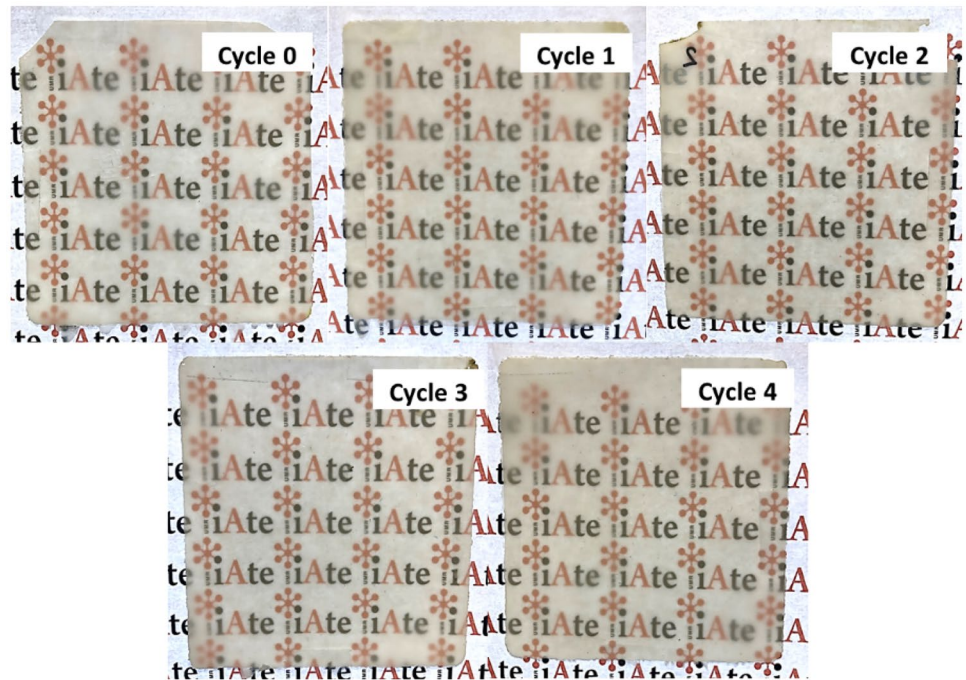


Table 2 Evolution of the mechanical properties after reprocessing cycles. Values represented are mean \pm standard deviation

Sample	Young modulus (MPa)	Tensile strength (Mpa)	Strain at break (%)
Cycle 0	1148 ^{ab} \pm 38	39.9 ^a \pm 1.5	6.2 ^a \pm 0.3
Cycle 1	1068 ^a \pm 59	40.0 ^a \pm 0.7	6.8 ^a \pm 0.2
Cycle 2	1143 ^{ab} \pm 57	38.4 ^{ab} \pm 1.8	6.4 ^a \pm 0.7
Cycle 3	1199 ^b \pm 61	36.0 ^b \pm 3.4	4.1 ^b \pm 0.5
Cycle 4	1197 ^b \pm 121	36.5 ^b \pm 2.5	4.7 ^b \pm 1.4

The letters a and b symbolize groups of significantly different values

polymers, mechanical properties of PHBV reflect a rigid and fragile behaviour from the first cycle. Over the processing cycles and especially after the third one, a slight increase in young's modulus ($\sim 4.8\%$) and a decrease in both tensile strength ($\sim 8\%$) and strain at break ($\sim 25.2\%$) were observed. These variations indicate a reprocessing-induced embrittlement of PHBV. Most studies about reprocessing of biopolymers such as PLA, PBS or PHB reported that thermal reprocessing results in no or low influence on Young's modulus, supposing that the value remains stable since the decrease of molecular weight is balanced by an increase of crystallinity [32, 33]. However, a gradual drop in the tensile strength and strain at break values are observed. In our case, the increase of crystallinity is less pronounced than the decrease of molecular weight, which may explain the slight variation of the Young's modulus, but the decrease in tensile

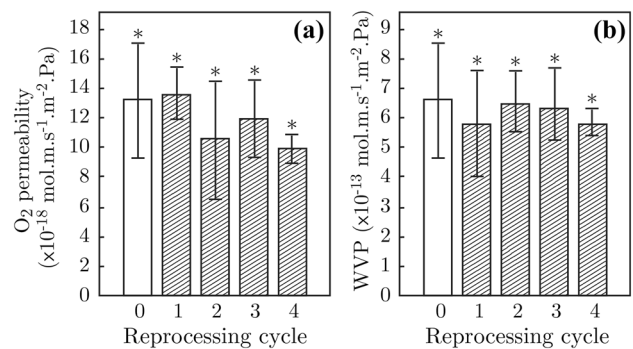


Fig. 2 Oxygen (a) and water vapour (b) permeabilities of PHBV films depending of the number of reprocessing cycles

strength and strain at break revealed a decrease of mechanical properties, due to the polymer chain scission.

Yet, these modifications being limited, the reprocessed materials present sufficiently preserved performances for the targeted applications. In reality, the stiffness of PHBV limits its applications to the packaging of solid food, as trays or jars.

Transfer Properties

Oxygen and vapour permeability measurements are considered as indicator of barrier properties that reflect the effectiveness of the packaging in extending the shelf life of the packaged product. Figure 2 shows the evolution of the oxygen and water vapour permeability of PHBV films over the

processing cycles, and demonstrates the lack of detrimental effect of the four successive reprocessing steps.

Oxygen permeability showed a slight downward trend although these variations are not significant. This is consistent with the slight increase of crystallinity (Table 1) as the permeation of molecules takes place in the amorphous phase. These values appear to be in agreement with previous measures reported on similar materials [34–36] and are characteristic of a good barrier material against gas and water vapour transfer, with low permeabilities (close to those of PET materials) [19]. A high variability of permeability measurements was observed which can be partially explained by the heterogeneity of the materials, induced during their thermoforming. It is worth noting that the small variation in material permeability (well below a factor of ten) does not impact the shelf life of the packaged food regardless of the system considered. Therefore, the reprocessing of PHBV did not have an influence on the performance of the packaging in terms of barrier properties.

Food Contact Suitability: Occurrence of Neo-formed Chemicals

As any material intended to come into contact with food, PHBV-based packaging must meet the inertness criteria defined in the European framework regulation (UE/1935/2004) and consequently must not transfer any substance that may present a danger for human health [22]. The issue of the suitability for food contact of a biosourced and biodegradable material such as PHBV cannot be raised on the same basis as a conventional plastic material since it is, in principle, free of additives. Therefore, compliance should be assessed on the unique basis of measuring the migration of non-intentionally added substances (NIAS). In the case of a compound present in the positive list of authorized substances (EU/10/2011), the migration of this substance must not exceed the specified specific migration limit that was set on the basis of toxicological data.

It is well-known that the thermomechanical degradation of PHVB obeys to random chain scission mechanism with crotonic acid (but-2-enoic acid) as one of the major low molecular weight degradation products [26, 27]. Crotonic acid is referenced in the positive list of authorized substances

with a specific migration limit (SML) of 0.05 mg/kg food (CE/10/2011) [22]. As consequence and although food-grade PHBV contains in principle a concentration of crotonic acid below the permitted threshold [37], the production and release of crotonic acid in food over reprocessing cycles must be considered as a critical point of safety concern. All the more so as oligomers may migrate and be hydrolysed (in vivo or ex vivo) then further exposure could occur. As PHBV is a rigid and stiff material, its application is a priori limited to rigid packaging such as trays and jars, mainly dedicated to solid foodstuff (e.g. meat, cheese, yogurts or dry food). To simulate the foodstuff that could be packed in PHBV, three food simulants have been selected, namely, ethanol 95% for fatty food, acetic acid 3% for acid food and Tenax for dry food [22]. Table 3 summarizes the specific migration of crotonic acid in the different food simulants as function of processing cycle number.

Migration of crotonic acid in 95% ethanol, increased with the number of processing cycles, reaching 0.042 mg/Kg after the fourth cycle. However, in both 3% acetic acid and Tenax, the amount of crotonic acid was barely detectable by the methods used with values below of 0.01 mg/Kg in acetic acid 3% and less than 0.001 mg/Kg in tenax. These results indicate that crotonic acid resulting from the thermomechanical degradation of re-processed PHBV (see Table 1 for chain scission) is readily released in 95% ethanol, whereas it does not migrate into aqueous acetic acid and even less into solid food simulant. This is consistent with previous safety assessment of poly(hydroxybutyrate-co-hexanoate) (PHBH) from EFSA, where the overall migration and the specific migration of crotonic acid were evaluated in various food simulant [38, 39]. Overall migration was found to be higher in 95% ethanol while it was lower in 3% acetic acid and not detectable in tenax. These results confirm the conclusion of Angelier et al. (2020) [40] that, based on global migration measurements, contact with ethanol 95% constitutes the worst conditions of use for PHBV-based materials. In addition, EFSA has issued an opinion stating that EtOH 95% is not a suitable food simulant for such polar polymers and that migration into it should not be considered since it essentially gives total extraction [38].

From a regulatory stand-point, the specific migration of crotonic acid proves not exceed the specific migration limit

Table 3 Specific migration of crotonic acid from processed PHBV into food simulants

Processed PHBV	Crotonic acid specific migration (mg/kg 95% ethanol)	Crotonic acid specific migration (mg/kg 3% acetic acid)	Crotonic acid specific migration (mg/kg tenax)
Cycle 0	0.015 ± 0.001	<0.01	<0.001
Cycle 2	0.018 ± 0.001	<0.01	<0.001
Cycle 4	0.042 ± 0.002	<0.01	<0.001

For 3% acetic acid and tenax measurement, the migration of crotonic acid was not detectable. Values are given as being below the detection limit of the method

of 0.05 mg/Kg in the three food simulants used in this study suggesting that, after four processing cycles, virgin PHBV (without additives) could be considered to have no health concerns. However, it is important to keep in mind that reprocessing of PHBV was conducted at laboratory small-scale and do not accurately reflect the industrial process conditions including, in particular, a potentially much longer residence time of the polymer in the extrusion chamber. As consequence, the values measured in food simulants must be regarded with care and attention as they could come alarmingly close to the SML after four processing cycles.

The assessment of the food contact suitability of PHA-based recycled materials is not currently covered by any EU directive or guidance from the European health authorities. For this reason, we need to be vigilant in assessing the risk associated with recycled PHBV materials by integrating the evaluation of neo-formed compounds and the evolution of inertness properties that evolve with the structural modifications generated by the thermal treatment cycles. We should not only apply the challenge test approach inspired by PET bottle-to-bottle recycling.

Conclusion

The prospect of recycling PHBV-based food packaging is an issue that requires the consideration of many criteria. The approach applied in this investigation is based on a comprehensive assessment of the impact of repeated extrusion-compression cycles (up to four cycles) on the functional properties and the safety (through the assessment of neo-formed products) of the resulting packaging. Gas and mass transfer properties are at the heart of these issues as they determine the barrier performance and the food contact suitability of recycled materials. Thermo-mechanical treatments applied to the material induce multiple structural modifications at the molecular level such as random chain scission and probable depolymerisation which need to be considered with respect to their effects on these transfer properties. While these macromolecular breakdowns induce a mechanical embrittlement of the material, they do not induce any significant variation of the water vapour and oxygen permeability values, which leads to the conclusion that multiple recycling does not dramatically change the usability of PHBV materials as food packaging for solid foodstuff (as trays and jars). Apart from market and infrastructure considerations, the main technological barrier to the deployment of mechanical recycling technology applied to PHBV-based food packaging is probably related to the release of the crotonic acid produced by the chain depolymerization and subject to a low migration limit. This point of concern is all the more important at a time when the European Commission is opening a consultation on a draft amendment to the

evaluation provisions for recycled plastic. The aim of this initiative is to extend the recycling of plastics intended to come into contact with food, currently restricted to PET, to other resins and thus to extend it to other packaging waste. The first draft submitted for public consultation proposes an evolution of provisions for the appropriate evaluation of non-PET materials including increased vigilance on residual incidental contamination. Unlike the challenge test procedure used for PET, which does not take into account the presence of neo-formed contaminants during the process, the future alternative approach is based on designed sampling strategy to obtain the best possible estimate of the average contaminant level in a batch of rec. The specific migration values of crotonic acid are highly dependent on the type of food and storage conditions. However, the thermal treatment applied to post-consumer PHBV packaging will have to be finely optimized in order to avoid any excessive production of crotonic acid within a concentration limit in the sample batch which is not defined at present.

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Declarations

Competing interests The authors declare that they have no competing financial interest of personal relationship that could influence the work reported in this paper.

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