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RESEARCH ARTICLE

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Development of extrusion blown films of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blends for flexible packaging

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Abstract

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biodegradable polymer with significant potential for use in food packaging. However, its limited melt strength poses a challenge when employing film-blowing techniques to produce flexible packaging. To overcome this obstacle, we developed blends consisting of 70 wt% PHBV and 30 wt% poly(butylene-co-succinate-co-adipate) (PBSA). Organic peroxides such as dicumyl peroxide and 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, were utilized as reactive compatibilizers to enhance the interfacial adhesion between the polymers. Additionally, acetyl tributyl citrate (ATBC) was employed as a plasticizer to improve processability and ductility. The inclusion of organic peroxides resulted in the formation of long-branched structures, as confirmed by the van-Gurp-Palmen plot. The melt flow index decreased from 30 to 9.8 g/10 min without ATBC and 15.5 g/10 min with ATBC. Successful production of blown PHBV/PBSA films was achieved on a pilot scale (bubble height 180 cm). These films exhibited heat-sealing capability and increased impact strength (7.7 kJ/m^2). Moreover, the films maintained a maximum elongation at break of 4% during a 3-month storage experiment with frozen food. Food safety was assessed through overall migration experiments, and the non-plasticized films received approval. In conclusion, the compatibilized PHBV/PBSA blends demonstrate great potential as materials for manufacturing film-blown flexible packaging.

KEYWORDS

biobased polymers, biodegradable polymers, compatibilizer, film blowing, food packaging, mechanical stability, polymer processing

1 | INTRODUCTION

Plastics possess outstanding material properties, including lightweight, low production cost, chemical resistance, ease of processing, versatility in shaping, and high thermal and mechanical properties. They find extensive use in various industrial sectors, with the packaging industry accounting for over 40% of plastic consumption. However, to reduce their environmental impact stemming from fossil fuel extraction and pollution associated with waste treatment, there is a growing need for plastics to incorporate renewable or alternative feedstocks like biomass or recycled plastics. Moreover, it would be environmentally advantageous if the end-of-life treatment of plastics shifted from incineration or landfill towards recycling or controlled biodegradation.[1]

In this regard, biopolymers offer a promising solution for circular bioeconomy, utilizing renewable feedstocks for material production and facilitating carbon return to the soil through biodegradation. Polyhydroxyalkanoates (PHAs) are a particularly excellent choice as they are produced by microorganisms and exhibit biodegradability in all natural environments, even in sea water.[1,2] Among the PHA family, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) along with its counterpart poly(3-hydroxybutyrate) (PHB) has already gained commercial availability, making it suitable for larger-scale applications, such as food packaging. However, these polymers face certain challenges, including a narrow processing window, low thermal stability, high crystallinity, and brittleness.[3] This brittleness arises from the glass transition temperature (T_g) being close to room temperature (0–5°C), secondary crystallization of the amorphous phase at room temperature, and the presence of interspherulitic cracks.[4]

One common and cost-effective strategy to address brittleness and improve processing ability by incorporation of plasticizers.[5,6] Plasticizers reduce the glass transition temperature and stiffness while enhancing the elongation at break by increasing the free volume[7] and modifying cooperativity scales in the amorphous phase.[8,9] They also act as processing aids by reducing melt viscosity.[10] Several plasticizers have been studied for PHBV and PHB, including Licowax®,[11] soybean oil (SO), epoxidized soybean oil (ESO),[12] phthalates,[13,14] polyethylene glycol,[12,15–17] oligomers,[18–20] and citrate esters such as triethyl citrate (TEC)[10,13,21] or acetyl tributyl citrate (ATBC).[10,12,15,22–24] The choice of a plasticizer depends on factors such as the intended application, miscibility with the polymer, thermal stability at processing temperature, and regulatory approval for food contact. The Hansen of Hildebrand solubility factors are a help for choosing a plasticizer molecule, because they predict miscibility and solubiliy.[25] The Hildebrandt solubility parameter of PHBV was reported between 18.5 and 20.1 $MPa^{1/2}$.[26,27] For example, the Hildebrandt solubility parameter of ATBC (between 18.7 and 20.2 $MPa^{1/2}$)[25,26] is close to PHBV; therefore good miscibility can be expected. ATBC is thus an interesting molecule, and gave promising results in already published studies.[10,12,15,22–24] Furthermore, it is authorized for food contact according to the European regulation (EN n° 10/2011 on plastic materials intended to come into contact with food).

Another approach to enhance PHBV's ductility and processability is blending it with flexible biodegradable polymers.[28] Significant research has been conducted using blends with poly(lactic acid) (PLA),[29–33] poly(butylene adipate-co-terephthalate) (PBAT),[34–38] poly(butylene succinate) (PBS),[39,40] or poly(butylene succinate-co-butylene adipate) (PBSA).[41–44] However, notable improvements in ductility were generally observed when PHBV was the minor constituent.[26,45] In blends based mainly on PHBV, the improvement was small.[35,42] Compatibilization between PHBV and the partner polymer is often required. Dicumyl peroxide (DCP), a free radical initiator, has been successfully employed as a reactive compatibilizer, easy to implement in reactive extrusion and very efficient to obtain PHB branching and/or crosslinking.[46] Crosslinking with the partner polymer in blends creates compatibilizer structures, which leads to decreased size of dispersed polymer nodules,[39] and increased toughness.[36,39,47,48] DCP induced reactions have been reported to enhance melt strength, which is beneficial for PHBV's processability and to improve impact strength.[28]

While extensive research has focused on developing PHBV-based materials for food packaging on the lab scale, only a few reports have addressed scalable processing techniques suitable for industrial production.[49] The low melt strength and viscosity of PHBV[3] make it advantageous for injection molding of articles like trays. However, flexible films are predominantly used in food packaging, and their production via film-blowing extrusion requires high melt strength and extensional viscosity. Only a limited number of studies have reported successful film blowing of PHBV.[49] Blends incorporating PHBV were a successful strategy for producing PHBV films due to improved melt strength.[34,36,45,50,51] For example, PBAT or poly(butylene sebacate-co-butylene terephthalate) improved the bubble stability.[36] In previous studies, we developed a PHBV/PBSA blend with a 70 wt % PHBV and 30 wt % PBSA ratio, compatibilized with DCP for extrusion blowing.[42,44] We successfully demonstrated the feasibility of the film blowing process

on the small laboratory scale using an optimal DCP content of 0.1 parts per hundred (phr). However, the extrusion blown bubble exhibited draw resonance, and the resulting films were relatively thick (approximately 100 μm).[44] The objective of the present work is to further optimize the blend composition by incorporating a plasticizer to enhance the final ductility of the blends. The extrusion blowing process will be scaled up to a small pilot scale. Based on a literature analysis, ATBC was chosen as the plasticizer. We showed already, in coherence with other studies, that the compatibilization of PHBV and PBSA is necessary to obtain blends with small PBSA droplets and ensure interfacial adhesion.[44] In September 2022, a change in the hazard classification by the European Chemicals Agency (ECHA) classified DCP (CAS 80–43-3) as having Reproductive Toxicity 1B. Consequently, it is no longer permitted for use in Food Contact Materials and needs to be replaced for this application. With that purpose, we choose LUPEROX® 101E (2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane), which is an alternative organic peroxide that complies with food safety regulations and can replace DCP as a compatibilizer in PHBV blends.

This article is divided into two parts. The first part focuses on optimizing the plasticizer content in the blends, starting with the previously determined blend composition and utilizing DCP. The impact of LUPEROX® on blend characteristics is evaluated on a small scale. The best formulations were then utilized for scaled-up blend production and film blowing extrusion on a small pilot scale. The properties of the resulting films, their safety, and their performance in contact with frozen food were subsequently investigated.

2 | MATERIALS AND METHODS

2.1 | Materials

Commercial PHBV (reference PHI 002) containing 1 mole percent of hydroxyvalerate (HV)[44] and PBSA (reference PBE 001) were purchased from NaturePlast (France). Polymers were dried at 70°C under vacuum for at least 6 h before use. Luperox® 101E (CAS 78–63-7, MW: 290.44, melting point: 8°C, boiling point: 56°C @ 7 mmHg, decomposition temperature around 170°C as per Arkema recommendations) was kindly provided by ARKEMA, dicumyl peroxide (DCP) (CAS 80–43-3, MW: 270.37, melting point: 40°C, boiling point: 130°C, decomposes) was purchased from ACROS and acetyl tributyl citrate (ATBC) (CAS 77–90-7, MW 402.48, melting point: 80°C, boiling point: 331°C) was purchased from Sigma-Aldrich (p.a. quality) and used as received.

2.2 | Blend formulations and nomenclature

The formulation was developed starting with a blend of PHBV/PBSA with a ratio of 70/30 wt/wt and 0.1 phr (parts per hundred of resin on a weight basis) DCP. The optimization of this formulation was reported in our earlier papers.[42,44] The ATBC was added to the PHBV/PBSA 70/30 blend with the appropriate mass. Because it diluted the blend, the mass percentage of PHBV and PBSA changed, but the ratio between both polymers was constant. The individual formulations are presented in the Table 1.

2.3 | Batch mixing

Polymers were dried at 70°C under vacuum for at least 6 h before use. The blends were mixed in an internal mixer SCAMEX Rheoscam (France) at 190°C and 90 rpm for 9 min. The PHBV was pre-melted for 6 min to obtain homogenous mixtures. PBSA pellets were mixed with DCP or Luperox® introduced in the batch mixer and the mixing was continued for 3 min. For the fabrication of plasticized blends, PHBV was pre-melted for 3 min, then ATBC was introduced and the mixing continued for 3 min. After that, PBSA mixed or not with DCP or Luperox® was added and the mixing continued for 3 min. The melt was pulled out of the batch mixer and cut into pieces. The pieces were stored in a desiccator over silica gel.

To obtain samples for thermal or mechanical testing, the blend pieces were molded by thermo-compression with the help of a thermal press (SCAMEX 15 T, France). The samples were sandwiched between two Teflon sheets and two metal plates. The sandwich was introduced in the press and pre-melt for 3 min without pressure. Then, the pressure was applied in two successive steps, at first 80 bar for 1 min and then 150 bar for 1 min. Aluminum foils of 200 μm were used as mold to obtain controlled thickness. The final thickness was measured with a micrometer.

2.4 | Compounding using twin screw extrusion

Compounding of plasticized and unplasticized PHBV/PBSA blends with Luperox® or DCP was carried out using a twin-screw extruder with a 16 mm diameter screw with a length to diameter ratio of 40 L/D (Thermo Haake Ptw 16-40D). The used configuration was co-rotating, intermeshing and interpenetrated screws. A photo of the screw set up is given in the supplementary

TABLE 1 Blend formulations and their nomenclature used in the work.

Sample	Process	Formulations			
Formulations with DCP		**PHBV (wt %)**	**PBSA (wt %)**	**DCP (phr)**	**ATBC (wt%)**
PHBV/PBSA/DCP	B	70	30	0.1	—
PHBV/PBSA/ATBC5/DCP	B	66.5	28.5	0.1	5
PHBV/PBSA/ATBC10/DCP	B, TSE	63	27	0.1	10
PHBV/PBSA/ATBC15/DCP	B	59.5	25.5	0.1	15
PHBV/PBSA/ATBC20/DCP	B	56	24	0.1	20
Formulations with Luperox®		PHBV (wt %)	PBSA (wt %)	Lp (phr)	ATBC (wt%)
PHBV/PBSA/0.1Lp	B	70	30	0.1	—
PHBV/PBSA/0.2Lp	B, TSE	70	30	0.2	—
PHBV/PBSA/ATBC10/0.1Lp	B	63	27	0.1	10
PHBV/PBSA/ATBC10/0.2Lp	B, TSE	63	27	0.2	10

Abbreviations: B = fabricated by batch mixer, TSE = fabricated by twin screw extrusion, phr based on the quantity of PHBV/PBSA blend, 1 phr is one part per hundred, meaning 1 g + 100 g blend, Lp = Luperox® 101E.

information. PHBV, PBSA and DCP or Luperox® were fed as hand-mixed dry blend with a pellet dosing unit (Thermo Haake metering feeder MF1, France) in the second entry of the extruder. Temperature profile was as follows:

- Barrel: Zone 1/2/3/4/5/6: 20°C/20°C/130°C/170°C/170°C+ Die: 170°C
- Screw speed: 300 rpm

For each formulation, the output flow rate was measured manually by weighting. ATBC was fed in the third entry at 113 g/h using a dispensing pump ISMATEC® REGLO-Z (Cole-Parmer GmbH, Germany). At the exit of the die, the rods were cooled on a conveyor belt and pelletized before being sealed in hermetic bag. The draw speed was adjusted in order to obtain a 3 to 4 mm diameter rod.

2.5 | Film blowing extrusion

A single screw extrusion equipped with a 25 mm diameter screw having a length to diameter ratio of 20 L/D (SCAMEX Rheoscam, France) and a helicoidal blown film die of 50 mm in diameter with a gap of 0.8 mm was used. The die was equipped with a 450 µm mesh size filter. Film blowing was realized using the film blowing extrusion device MAPRE/COLLIN (Belgium). The temperature profile was as follows:

- Barrel: Zone 1/2/3/4/5/6/7: 140°C/160°C/170°C/170°C/180°C/180°C/170°C
- Die: Zone 1/2/3/4: 170°C/165°C/165°C/165°C
- Screw speed: 30 rpm.

The cooling was realized by applying air at the base of the bubble and the drawing rolls were placed at around 1.5 m from the die in order to leave the time to cool the material to avoid welding. The blowing of the bubble was adjusted manually by compressed air inside the bubble until reaching a stable bubble. Once the bubble stabilized, the process was run for approximately 15 min. The flat diameter of the bubble was measured using a ruler at regular points over 1 m. Movies of the film blowing process are provided in the supplementary information.

2.6 | Characterization techniques

2.6.1 | Molar mass averages by size-exclusion chromatography

Size-exclusion chromatography (SEC) was performed using a Gilson pump (France) coupled to a Waters autosampler and refractometric index detector (Waters, France). The separation was carried out on a system consisting of a guard column (PLgel 5 µm) and three columns (two columns PLGel 5 µm MIXED-C and one column PLgel 3 µm MIXED E, Agilent Technologies) maintained at 40°C in a column oven (Waters, France). The flow rate of the solvents THF (for PBSA) and $CHCl_3$ (for PHBV) was 1 mL/min. The calibration curve was established for each solvent using three standard kits (EasiVials, 2 mL) containing each four narrow polystyrene standards of molecular weight between $4.69{\cdot}10^3$ and $5.68{\cdot}10^6$ g/mol (Agilent Technologies). Data treatment

were done using Empower 3 software (Waters). The sample preparation involved grinding the blends under liquid nitrogen and dissolving PBSA in THF (approximately 10 mg/mL) at room temperature without stirring for 2 h followed by dissolving PHBV in boiling $CHCl_3$ (approximately 10 mg/mL) for 12 h. The supernatant was sampled after sedimentation of the insoluble phase and filtered before analysis with the help of 0.45 μm Teflon syringe filters. All sample preparations were done in duplicate.

2.6.2 | Gel content

The PHBV/PBSA 70/30 blends were ground into fine powders using a ball mill under liquid N_2 (Model Retsch MM400, Germany). Two successive Soxhlet extractions were performed to separate PHBV and PBSA. The Soxhlet filters and the samples were dried and weighted. PBSA was dissolved in THF under reflux for approximately 4 h. THF does not dissolve PHBV. After the extraction of PBSA, the remaining PHBV in the Soxhlet filter was dissolved using $CHCl_3$ under reflux overnight (approximately 18 h). The Soxhlet filter containing the insoluble polymer gel was dried and weighted. The gel fraction was calculated as follows:

$$gel\,wt.\% = \frac{m_1}{m_0}.100\% \tag{1}$$

where m_0 is the original weight of samples and m_1 is the weight of dry residues obtained after dissolution. The analysis was carried out in duplicate.

2.6.3 | Rheological properties

The melt flow index (MFI) of the PHBV/PBSA blends was measured according to the ISO 1133 standard procedure using a MFI 4106 device (Zwick, Germany). The samples were extruded through the die under a constant load of 2.16 kg at 190°C, and the MFI was expressed as the mass passing through the die during a period of 10 min (g/10 min). Measurements were done in triplicate. Rheology measurements in melt state were performed with a stress-controlled rheometer (MCR 302, Anton Paar, Graz, Austria) using a disk-shaped specimen. A parallel-plate geometry was used with a gap set between 750 and 800 μm at 185°C. Dynamic frequency sweep experiments were performed from 0.01 to 100 Hz in the linear viscoelastic region. The signals of the phase angle and the viscoelastic moduli were recorded.

2.6.4 | Thermal properties

Thermal properties of blends were assessed by DSC (DSC1, Mettler Toledo, Switzerland) according to the program shown in Figure 1. All measurements were done in triplicate under N_2 (flow rate 50 mL/min) with 5 to 10 mg of materials sealed in 40 μL aluminum pans. Calibration was carried out with Indium and Zinc standards. The first cooling and second heating scan served to measure the crystallization and melting enthalpy. The erasing of thermal history of the polymer blends enabled to gather more reproducible data and to compare more rigorously the properties of the blends which were obtained using different processing methods. The T_g of PHBV was measured at the 3rd heating scan after physical aging at −10°C and the T_g of PBSA at the 4th heating scan after physical aging at −40°C.

The crystallinity each polymer $\{\chi_i\}_{i=PHBV,PBSA}$ was determined from the endotherm $\Delta H_{m,i}$ as:

$$x_i = \frac{\Delta H_{m,i} - \Delta H_{cc,i}}{w_i \Delta H^0_{m,i}}, \tag{2}$$

where w_i is the weight percentage (wt%) of the corresponding polymer, $\Delta H_{cc,i}$ the cold crystallization enthalpy and $\Delta H^0_{m,i}$ the melting enthalpy of a 100% crystalline material with pure PHBV (146 J/g, from([52] and PBSA (113.4 J/g, from).[53]

2.6.5 | Scanning electron microscopy

The morphology of the PHBV/PBSA blends was analyzed using Environmental Scanning Electronic Microscopy (ESEM) technology on a FEI Quanta 200 instrument, with an accelerated voltage of 12 kV. The samples were sputter-coated with a thin gold layer using an Emitech K550 Sputter coater. Images were acquired at the cryo-fracture edge of the sample or at the fracture surface after tensile testing.

2.6.6 | Mechanical properties

Tensile properties were measured using dumbbell-shaped samples of type 5 with a target thickness of 200 μm which were cut from the compression-molded sheets. The sample thickness was set from the average of five measurements measured with a caliper. At least ten samples were tested for each blend composition.

Tensile tests were conducted under ambient and freezer (−20°C) temperatures. At ambient temperature,

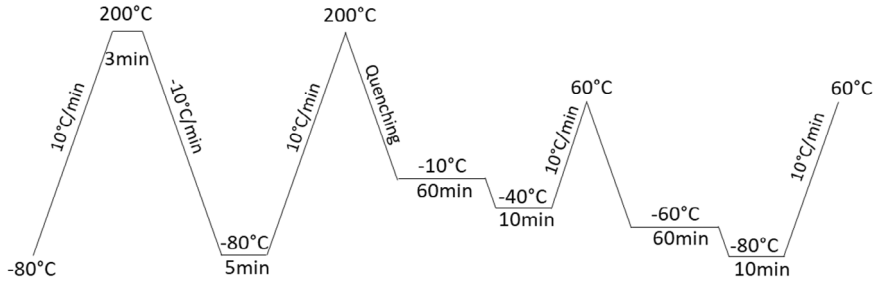

FIGURE 1 Differential scanning calorimetry measurement protocol.

tensile properties were measured using a texture analyzer (model TAHD, Stable Micro Systems, UK) equipped with pneumatic grips and with a 5 mm/min crosshead speed. At freezer temperature (−20°C), tensile tests were performed on a Zwick Z010 instrument (Zwick, Ulm, Germany) with the same crosshead speed.

Unnotched Charpy impact tests were performed according to the ISO 179 standard test method using a Zwick B5113.300 impact tester. Pendulums of 1 and 4 J were used for PHBV-based blends and PBSA, respectively. A minimum of five samples were tested for each mechanical test and blend formulation.

2.6.7 | Packaging tests and aging in food contact

Physical aging was conducted on PHBV-based bags upon various storage times at −20°C and containing parfried frozen French fries (product reference "frites Tradition", McCain, France). The bags were created using blown extrusion film that was cut to a length of 30 cm and thermo-sealed manually on one side using a vacuum packing machine (Model C200, Multivac, Germany) with a sealing time of 0.8 s. The bags were then filled with 625 g of parfried frozen French fries and sealed on the other side. The samples were stored in a freezer at −20°C for 3 months. After that, the bags were taken out from the freezer and cut open to discard the food. The test specimens were cut out of the opened bags. They were conditioned at 25°C and 50% RH for a minimum of 24 h. Tensile tests were carried out using a Zwick Z010 instrument with a crosshead speed of 5 mm/min.

2.6.8 | Overall migration tests

The overall migration was measured by the laboratory LNE (Trappes, France) using the gravimetric method according to the European Regulation n° 10/2011 (Commission Regulation EU n° 10/2011 of 14 January 2011 on Plastic Materials and Articles Intended to Come into Contact with Food, 2011). The test was carried out in isooctane, a validated alternative for the food simulant D2 and in ethanol/water 50/50 vol%, food simulant D1. Both food simulants are recommended for fatty foods and processed vegetables in oily medium. They were chosen with respect to the application of packaging of French fries. The films were immersed in the food simulant respecting the ratio 1 dm^2 polymer/1 kg food simulant. The test temperature was 40°C and the time 10 d. This condition simulates storage of food at room temperature for 1 year. After the test time, the films were withdrawn and the food simulant evaporated on a heating plate. The residue was weighted. The overall migration was determined as the residual mass per surface of polymer:

$$M = \frac{m_2 - m_1}{S}, \tag{3}$$

where M is the overall migration in milligrams per dm^2, m_1 is the weight of the glass vial before overall migration, m_2 is the weight of the glass vial after overall migration and S is the area of the polymer (taking into account the both sides and neglecting the borders).

3 | RESULTS AND DISCUSSION

3.1 | Development of PHBV/PBSA blends using the batch mixer

3.1.1 | Preparation of the sample set by batch mixing

The formulation of the PHBV/PBSA blends was built upon the findings from our previous study, which assessed the feasibility of film blow extrusion on a small lab-scale equipment.[44] To enhance the processing ability and ductility of the blends, ATBC was incorporated as a plasticizer. Figure 2a illustrates the torque changes recorded within the mixing chamber during the melt blending of PHBV and PBSA, with the addition of both DCP and ATBC. The first decrease of torque starting after 50 s corresponded to the melting of PHBV. The inclusion of ATBC (200 s) into the pre-melted PHBV resulted in a

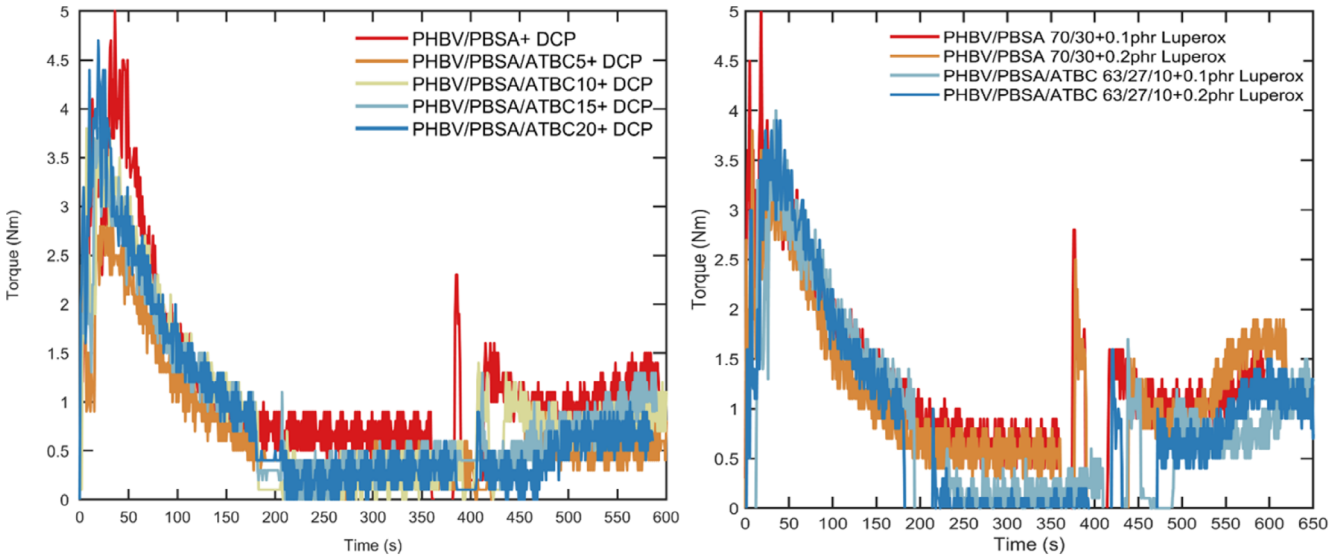

FIGURE 2 Evolution of the torque during melt mixing of PHBV/PBSA blends: (a) blends containing 0.1 phr DCP and different ATBC concentrations; (b) blends containing Luperox® and ATBC. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Gel content and molar mass averages of PHBV/PBSA blends with DCP, Luperox® and ATBC obtained by batch mixing.

		PHBV			PBSA		
Samples	**Gel content (%)**	M_n	M_w	$Đ$	M_n	M_w	$Đ$
PHBV ref.[44]	2 ± 2	n.p	n.p	n.p			
PHBV ref.[54]		113,000	290,900	2.6			
PBSA ref. [44]	1 ± 1				140,000	204,600	1.5
PHBV/PBSA/DCP	9 ± 4	79,800	149,100	1.8	10,200	21,500	2.1
PHBV/PBSA/ATBC5/DCP	8 ± 1	56,700	105,700	1.9	43,300	133,700	3.1
PHBV/PBSA/ATBC10/DCP	5 ± 1	49,000	104,000	2.1	28,300	100,500	3.6
PHBV/PBSA/ATBC15/DCP	11 ± 4	62,200	116,200	1.9	30,000	93,400	3.1
PHBV/PBSA/ATBC20/DCP	13 ± 3	73,400	134,100	1.8	7100	15,100	2.1
PHBV/PBSA/0.1Lp	20 ± 5	84,900	147,000	1.7	21,400	76,700	3.6
PHBV/PBSA/0.2Lp	28 ± 2	91,200	180,000	2.0	14,800	31,800	2.1
PHBV/PBSA/ATBC10/0.1Lp	15 ± 1	67,500	166,400	2.5	n.p.	n.p.	
PHBV/PBSA/ATBC10/0.2Lp	19 ± 1	68,700	160,100	2.3	n.p.	n.p.	

Note: Neat polymer data were measured on initial pellets and published in ref.,[44] n.p. not present, PHBV molar mass data obtained from ref.[54]

reduction in torque compared to the melt without plasticizer. This was attributed to the role of plasticizers as dilutants, leading to a decrease in melt viscosity. After 360 s, PBSA and DCP were introduced (second peak-like increase). The torque first decreased because of the melting of PBSA and then increased because of the introduction of DCP. DCP, acting as a free radical initiator, initiating chain extension and cross-linking reactions in both PHBV and PBSA. ATBC decreased the final torque, but its value was not correlated to the ATBC content.

In Figure 2b, the torque evolution during the melt mixing of the PHBV/PBSA blend using Luperox® and ATBC is displayed. After the introduction of PBSA and Luperox®, there was a sudden rise in the torque curve, presumably due to chain extension and crosslinking reactions occurring in PHBV and PBSA.

3.1.2 | Analysis of macromolecular weight averages and gel content of compatibilized blends

The impact of DCP, Luperox®, and ATBC on the macromolecular chain length was assessed through size

exclusion chromatography, and the findings are summarized in Table 2. The data for the raw materials were taken from our previous publication.[44] The initial macromolecular mass of PHBV could not be analyzed because it was very difficult to dissolve and the concentration in solution was below the detection limit of our apparatus. For comparative purposes, we included literature data for PHBV from the same supplier.[54] Our observed results exhibited a degradation of PHBV likely attributed to the batch mixing process. Thermal degradation during processing is a well-known concern for PHBV, involving random scission through β-hydrogen elimination, even at temperatures close to its melting point.[3,21,55] Chain extenders are typically employed to counteract such chain scission.

Relative to the literature value for PHBV's macromolecular mass, both DCP and Luperox® could not preserve PHBV's chain length in our process, although Luperox® displayed comparatively higher efficiency than DCP. The incorporation of ATBC also negatively influenced the macromolecular chain length. In comparison to PHBV, PBSA exhibited an even more pronounced decrease in its macromolecular mass averages. The increased dispersity value (above 2) for PBSA was characteristic of random chain scission. It's possible that our drying protocol was not stringent enough to prevent thermo-hydrolysis of PBSA at the relatively high process temperature required for PHBV melting. The absence of the PBSA peak in chromatograms of formulations containing Luperox® and ATBC might be caused by a decrease of the dissolved quantity in the measurement range caused by higher gel content and important chain degradation. The relatively low protection of PBSA against degradation suggests that the action of DCP or Luperox® likely took place predominantly within the PHBV phase.

To gauge the extent of cross-linking reactions involving PHBV and PBSA, the gel content of the blends was measured (as shown in Table 2). The addition of free radical initiators led to an increase in gel content, indicating their role as crosslinkers. Notably, blends containing Luperox® exhibited higher gel content compared to DCP blends, suggesting a more efficient cross-linking reaction. One, but not the unique reason could be that it was easier to homogeneously mix Luperox® with the PBSA pellets, because it is a liquid at room temperature, while DCP is a fine powder. The gel content of PHBV/PBSA/DCP blends with varying ATBC quantities remained relatively stable. The addition of ATBC to Luperox® containing blends reduced the gel content, likely due to a dilution effect. However, the gel content was still higher than that observed in blends containing DCP.

3.1.3 | Effect of ATBC on the thermal properties of DCP compatibilized blends

The thermal characteristics of the PHBV/PBSA/DCP blends, which were plasticized with ATBC, are outlined in Table 3. The thermal history of the samples was erased to compare uniquely the effect of formulation. Typical thermograms can be found in the supporting information. Notably, PHBV and PBSA are immiscible, a point that has been previously documented.[42] Consequently, distinct signals were discernible for each polymer phase. Concerning the PHBV phase, the crystallization temperature exhibited a shift towards lower values, a phenomenon frequently observed in plasticized PHBV.[21] The presence of ATBC at concentrations below 20 wt% did not impact the crystallinity degree of PHBV. Alike, the concentration of ATBC did not induce changes in the PBSA crystallinity degree. The melting temperature of PBSA crystals in plasticized blends displayed a shift towards cooler temperatures, indicative of thinner lamellae.[13] However, in the present scenario, the PBSA experienced significant degradation (Table 2), which could also cause distinct crystallization temperatures. Therefore, we cannot ascertain whether the decrease in crystallization temperature was driven by polymer degradation or plasticization.

The decrease of the glass transition temperature of PBSA and PHBV (numerical data in Table 3) was analyzed the empirical Fox equation. In absence of a detailed solubility analysis of ATBC in the different polymers, we supposed that ATBC would be partitioned equally in either phase without preference for one polymer:

$$\frac{1}{T_{g,i}} = \frac{w_{1,i}}{T_{g1,i}} + \frac{1 - w_{1,i}}{T_{g2}}, \tag{4}$$

where $T_{g1,i}$ is the glass temperature of PHBV or PBSA phase, T_{g2} is the glass temperature of ATBC (82.6°C), while $w_{1,i}$ is the weight fraction of PHBV or PBSA phase. The T_g of the PHBV phase is shown Figure 3a. It leveled off at about −4°C. On the contrary, Martino et al.[15] observed in their study that PHBV containing 10 wt % ATBC had a T_g of −14 °C, aligning well the prediction from Fox's equation (Figure 3a). Apparently, ATBC did not exhibit a preference for the PHBV phase. The T_g of PBSA was coherent with the prediction of Fox's law (Figure 3b), which corroborates the hypothesis that ATBC was preferentially solubilized in the PBSA phase. A part of the T_g depression of PBSA could nevertheless also be caused by the large decrease in macromolecular mass. If the total quantity of ATBC would have been partitioned to PBSA, its effective concentration in that phase

TABLE 3 Thermal properties of plasticized PHBV/PBSA blends with 0.1 phr DCP and ATBC evaluated by DSC from the first cooling scan (crystallization behavior), second heating scan (melting behavior) and the heating scan after physical aging of PHBV or PBSA (T_g).

	T_m (°C)		χ (%)		T_c (°C)		T_g (°C)	
	PHBV	PBSA	PHBV	PBSA	PHBV	PBSA	PHBV	PBSA
PHBV	171 ± 3	88 ± 3	68 ± 1		122 ± 1		2.4 ± 0.4	
PBSA				45 ± 4		38 ± 3		−45.9 ± 1.6
PHBV/PBSA/DCP	169 ± 1	85 ± 1	63 ± 2	29 ± 5	117 ± 1	54 ± 1	−1.1 ± 0.7	−48.9 ± 1.3
PHBV/PBSA/ATBC5/DCP	165	76	61	31	113	53	−4.1	−52
PHBV/PBSA/ATBC10/DCP	168	75	63	35	111	52	−4.2	−52.6
PHBV/PBSA/ATBC15/DCP	167	76	62	45	107	50	−3.3	−52.2
PHBV/PBSA/ATBC20/DCP	166	74	70	41	109	51	−3.9	−55.6

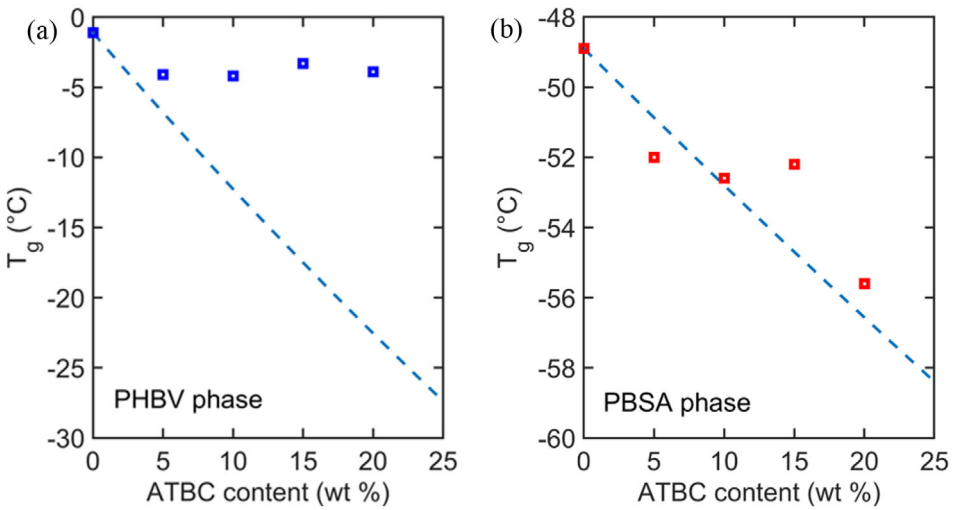

FIGURE 3 Glass transition temperature of the two distinct phases, (a) PHBV and (b) PBSA in PHBV/PBSA blends with 0.1 phr DCP as a function of ATBC content and modeling with Fox's law. Experimental results (empty symbols) and Fox equation (dashed line). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Mechanical properties of plasticized PHBV/PBSA blends with 0.1 phr DCP and ATBC.

Materials	Young modulus (MPa)	Maximum stress (MPa)	Elongation at break (%)
Neat PHBV[a]	3485 ± 60	22 ± 2	0.98 ± 0.1
Neat PBSA[a]	332 ± 8	15 ± 1	134.8 ± 48
PHBV/PBSA[a]	2227 ± 110	19 ± 2	1.5 ± 0.4
PHBV/PBSA/DCP	1973 ± 124	21 ± 3	1.9 ± 0.2
PHBV/PBSA/ATBC5/DCP	1114 ± 73	12 ± 2	2.0 ± 0.5
PHBV/PBSA/ATBC10/DCP	783 ± 83	11 ± 2	2.9 ± 0.9
PHBV/PBSA/ATBC15/DCP	703 ± 77	9 ± 2	2.4 ± 0.7
PHBV/PBSA/ATBC20/DCP	663 ± 75	8 ± 1	2.2 ± 0.3

[a]Blank values were taken from our earlier work ref. [42]

would increase. For example, the calculated ATBC concentration in the formulation containing 63 wt% PHBV, 27 wt% PBSA and 10 wt% ATBC would be 37 wt%. For this concentration, the Fox equation predicts a T_g at −62°C. All measured T_g values of PBSA where higher than that, which showed that there was most likely phase separation of ATBC in the blends.

3.1.4 | Effect of ATBC on tensile properties of DCP compatibilized blends

The change in mechanical behavior of PHBV/PBSA/DCP blends with different concentrations of ATBC is reported in Table 4. The blending of PHBV with PBSA yielded in materials with decreased stiffness and maximum yield

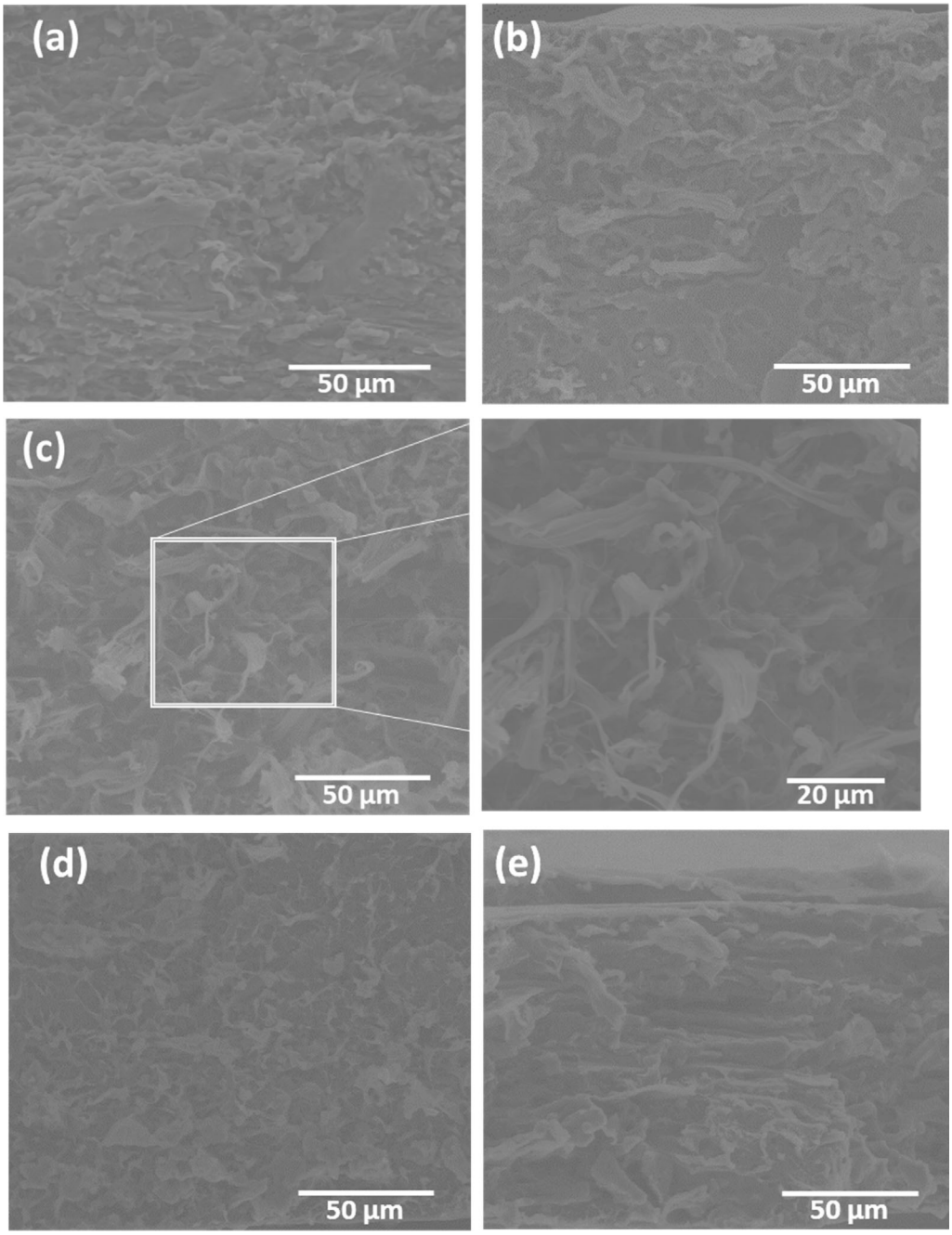

FIGURE 4 SEM images of the cross-section after tensile test of unplasticized and plasticized PHBV/PBSA/DCP/ATBC with ATBC content of (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt %.

strength, but did not increase the elongation at break. The compatibilization by DCP decreased a bit Young's modulus, but the material remained very brittle having low elongation at break. The brittleness is inherent to the PHBV spherulites with low percentage of HV. It is caused by the cold crystallization of the residual amorphous phase during storage at ambient temperature, and radial or circumferential cracks that can form inside spherulites of PHBV.[4,56] The introduction of ATBC as a plasticizer resulted in a reduction in stiffness, primarily observed by the diminished values of Young's modulus and maximum stress. Notably, at an ATBC concentration of 5 wt%, both Young's modulus and maximum stress underwent a reduction of 50%. For ATBC concentrations exceeding 5 wt%, alterations were marginal or negligible. Correspondingly, the elongation at break demonstrated a slight enhancement, reaching a maximum value of 2.9%. This result is in accordance with the results of Martino et al.[15] They reported that PHBV/ATBC blends with 5 wt% ATBC (near our effective plasticizer content) had a

TABLE 5 Thermal and mechanical properties of plasticized PHBV/PBSA blends with 10 wt% ATBC10 containing Luperox® measured by DSC at the cooling scan (crystallization behavior), second heating scan (melting behavior) and the heating scan after physical aging of PHBV or PBSA (T_g) and by tensile testing.

	T_m (°C)		T_c (°C)		χ(%)		T_g (°C)		Young modulus (MPa)	Maximum stress (MPa)	Elongation at break (%)
Samples	**PHBV**	**PBSA**	**PHBV**	**PBSA**	**PHBV**	**PBSA**	**PHBV**	**PBSA**			
PHBV/PBSA	169 ± 2	86 ± 2	117 ± 1	50 ± 1	67 ± 2	33 ± 5	−1.5 ± 0.1	−48.6 ± 2	2227 ± 108	19 ± 2	1.5 ± 0.4
PHBV/PBSA/ DCP	169 ± 1	85 ± 1	117 ± 1	54 ± 1	63 ± 2	29 ± 5	−1.1 ± 0.7	−48.9 ± 1.3	1973 ± 124	21 ± 3	1.8 ± 0.2
PHBV/PBSA/ ATBC10/DCP/	168 ± 1	75 ± 1	111 ± 1	52 ± 1	63 ± 2	35 ± 5	−4.2 ± 0.7	−52.6 ± 1.3	783 ± 83	11 ± 2	2.9 ± 0.9
PHBV/ PBSA/0.1Lp	170 ± 1	85 ± 1	115 ± 1	52 ± 1	63 ± 2	38 ± 5	−1.3 ± 0.1	−47.1 ± 0.1	1968 ± 146	18 ± 3	1.5 ± 0.3
PHBV/PBSA/0.2 Lp	169 ± 1	83 ± 1	116 ± 1	52 ± 1	61 ± 2	35 ± 5	−0.8 ± 0.1	−48 ± 0.8	1942 ± 129	19 ± 2	2.3 ± 0.7
PHBV/PBSA/ ATBC10/0.1Lp	162 ± 1	81 ± 1	111 ± 1	52 ± 1	61 ± 2	39 ± 5	−4.4 ± 0.1	−53.4 ± 0.1	942 ± 62	11 ± 3	2.5 ± 0.9
PHBV/PBSA/ ATBC10/0.2Lp	160 ± 1	78 ± 1	109 ± 1	50 ± 1	57 ± 2	40 ± 5	−2.8 ± 0.4	−52.9 ± 0.6	1001 ± 140	14 ± 2	4 ± 1

Young modulus of 1.7 GPa, tensile strength of 27 MPa and approximately 3.5% elongation at break. The small elongation at break of plasticized PHBV is consistently documented by numerous publications reporting values around approximately 1%.[21,57,58] Even plasticized, the PHBV blends remain brittle due to the inherent brittleness of the PHBV spherulites.

SEM analysis (Figure 4a-e) revealed noticeable alterations in the fracture surface of the samples due to compatibilization. This manifested in the presence of elongated fibers, most probably formed by PBSA or compatibilized PBSA/PHBV. It is noteworthy that similar morphologies resulting from polymer blend formulations with DCP have been documented in previous studies.[38,44] Introducing ATBC increased the elongation of these fibers, with the most extended stretched fibers observed at a concentration of 10 wt % (Figure 4c).

In summary, the concentration of 10 wt% ATBC emerged as the optimal choice, resulting in the reduction of T_g to −4.2°C, the enhanced mechanical properties (most significant elongation at break and substantial reduction in stiffness), and the comparatively extended length of the stretched fibers protruding from the fracture surface.

3.2 | Evaluation of the thermal and mechanical properties of the optimum blend formulation using Luperox®

The properties of the blends containing 10 wt% ATBC using Luperox® instead of DCP are reported in Table 5. We analyzed the data after erasing the thermal history to be able to compare the effect of Luperox® and ATBC on the thermal properties without the influence of the thermal history. The melting and crystallization temperatures, as well as the crystallinity degree, remained essentially unchanged compared to DCP-compatibilized blends. No significant distinctions were observed between the effects of 0.1 and 0.2 phr Luperox®. The T_g values for PHBV and PBSA also demonstrated similarity, except for the T_g of PHBV/PBSA/10ATBC/0.2Lp, which was elevated by approximately 1°C. This can potentially be attributed to local heterogeneities. In the case of non-plasticized PHBV/PBSA blends, both the Young's modulus and maximum stress matched that of PHBV/PBSA/DCP blends. The elongation at break exhibited an increase with higher quantities of Luperox®. Notably, the Young's modulus of the plasticized PHBV/PBSA blend with Luperox® surpassed that of blends with DCP. Moreover, an increased amount of Luperox® showcased a favorable impact on maximum stress and elongation at break. In combination with ATBC, Luperox® seemed to act more effectively as a crosslinker and/or chain extender compared to DCP. This suggests its viability as a DCP substitute in blends aimed for application in food packaging.

Considering these factors, the quantity of 0.2 phr Luperox® was selected for the scale-up experiments. For the sake of comprehensive comparison, the initial PHBV/PBSA/DCP formulation was also investigated, as it aligns with the majority of literature reports utilizing DCP.

TABLE 6 Output flow of the blends during twin screw extrusion and melt flow index.

Materials	Output flow (g/h)	MFI (g/10 min) (190°C, 2.16 kg)
Neat PHBV[a]	—	30 ± 1
Neat PBSA[a]	—	2.5 ± 0.7
PHBV/PBSA[a]	—	45 ± 1
PHBV/PBSA/DCP	1080	17.3 ± 0.1
PHBV/PBSA/0.2 phrLp	792	9.8 ± 0.3
PHBV/PBSA/ ATBC10/0.2phrLp	1130	15.5 ± 0.3

[a]Data for comparison, first published in ref.[44]

3.3 | Processability of optimized compatibilized and plasticized PHBV/PBSA blends at the small pilot scale

3.3.1 | Melt rheology of blends produced by twin screw extrusion

Compounds of PHBV/PBSA/DCP and plasticized and not plasticized PHBV/PBSA/0.2Lp were prepared using twin screw extrusion. The behavior of the extruded rod did not change among formulations. The output flow and the melt flow index are reported in Table 6. The output flow of the blend containing Luperox® without plasticizer was lower, because of higher torque build up in the twin screw extruder. This is correlated to the values of the MFI. The compatibilization of PHBV and PBSA with DCP or Luperox® decreased the MFI, which is indicative of higher melt strength obtained by chain extension and/or crosslinking reactions. The addition of ATBC increased the MFI, as expected, because plasticizers decrease the melt viscosity. The same observations can be made on the viscosity curves (Figure 5a) at low frequencies.

The crosslinking reaction in the compatibilized blends was already evidenced by the high gel content (Table 2). Figure 5a shows the evolution of the complex viscosity of the formulated PHBV/PBSA blends as a function of frequency in comparison to the non-compatibilized blend. The use of DCP or Luperox®, which are free radical

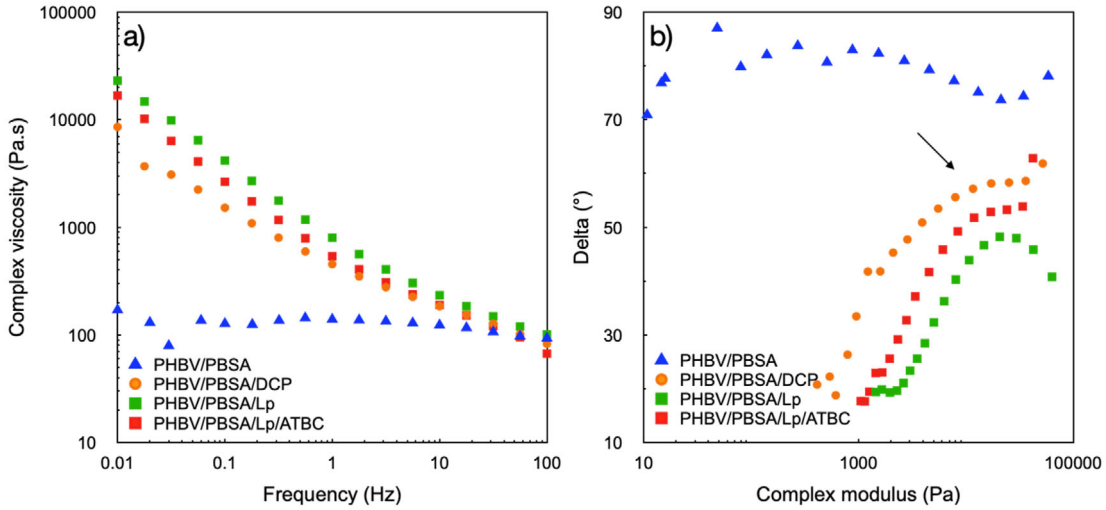

FIGURE 5 Rheological properties of PHBV/PBSA (70/30) blends: (a) evolution of the complex viscosity at 185°C as function of frequencies PHBV/PBSA containing 0.1 phr DCP or 0.2 phr Luperox® or 0.2 phr Luperox® and 10 wt% ATBC; (b) van Gurp – Palmen plot of PHBV/PBSA blends; data of PHBV/PBSA were first published in ref.[44] The arrow indicates the characteristic bump of long-chain branched macromolecules. [Color figure can be viewed at wileyonlinelibrary.com]

initiators,[39,59,60] caused the change from Newtonian to shear thinning behavior. This change can be characteristic of chain branching,[59] and the upswing of the complex viscosity at low frequency can be a consequence of crosslinking. Long chain branching is generally difficult to evidence. The van Gurp-Palmen plot, which plots the phase angle as a function of the complex modulus, can be used to classify specific macromolecular architectures.[61] It is illustrated in Figure 5b. We present the non-reduced plot, since it was difficult to obtain stable values of the shear moduli in the plateau region because of the degradation of PHBV. The PHBV/PBSA blend showed the signature of linear polymer chains (stable phase angle over the investigate range of complex moduli).[61] The blends containing Luperox® or DCP showed a bump at high modulus (high frequency, indicated by the arrow). This pattern is characteristic of a mixture of linear macromolecules and macromolecules with long-chain branching.[61] Inclusion of 10 wt% ATBC decreased the viscosity (Figure 5a) and moduli (Figure 5b, shift of the curves to the right), but the blend still featured the same characteristic pattern of a mixture of linear long-chain branched macromolecules. This was positive for the melt strength (Table 6) and opened the possibility of film blowing extrusion of PHBV-based blends.

3.3.2 | Film blowing extrusion of optimized PHBV/PBSA blends

The film blowing extrusion on the small pilot scale equipment with a bubble height of approximately 180 cm was possible for all three formulations (PHBV/PBSA/DCP, PHBV/PBSA/Lp, PHBV/PBSA/ATBC10/0.2Lp). The optimization of the process parameters was done manually until the bubble was stable. The Blow Up Ratio (BUR) and Draw Down Ratio (DDR) were calculated using the dimensions of the stabilized bubble using equation 5 and equation 6, respectively:

$$Blow\ Up\ Ratio\ (BUR) = \frac{R}{R_o} \tag{5}$$

$$Draw\ down\ ratio\ (DDR) = (Die\ gap / Film\ thickness) / BUR \tag{6}$$

where R and R_o are the bubble and the die diameter. Table 7 reports on the processing parameters. A feasibility test of film blowing of PHBV/PBSA/DCP was done previously on the small scale (bubble height 30 cm).[44] The film blowing ability of PHBV blends with a majority of PHBV could be confirmed here at the larger scale (Figure 6). The BUR of PHBV/PBSA/DCP was equal to that obtained at the smaller scale (3.2 in ref.,)[44] but the films were still relatively thick and presented thickness heterogeneities.

Figure 6 illustrates the successful film blowing extrusion process of PHBV/PBSA blends with Luperox®. When the film thickness of PHBV/PBSA/0.2Lp fell below approximately 60 μm, the extruded film exhibited a high degree of stickiness at the moment of bubble collapsing, resulting in inflation problems and instabilities (Figure 6a). In contrast, the PHBV/PBSA/ATBC10/0.2Lp

TABLE 7 Film blowing parameters of the optimized PHBV/PBSA blends with DCP, Luperox® and 10 wt% ATBC.

	PHBV/PBSA/DCP	PHBV/PBSA/0.2Lp	PHBV/PBSA/ATBC10/0.2Lp
Die diameter	50 mm		
Die gap	0.8 mm		
Film thickness	141 ± 66 µm	77 ± 11 µm	88 ± 11 µm
Flat bubble diameter	85 ± 4 mm	153 ± 2 mm	194 ± 2 mm
Blow up ratio (BUR)	1.7	3.1	3.9
Draw down ratio (DDR)[a]	3.2	3.4	2.6

[a]Based on the average value of film thickness.

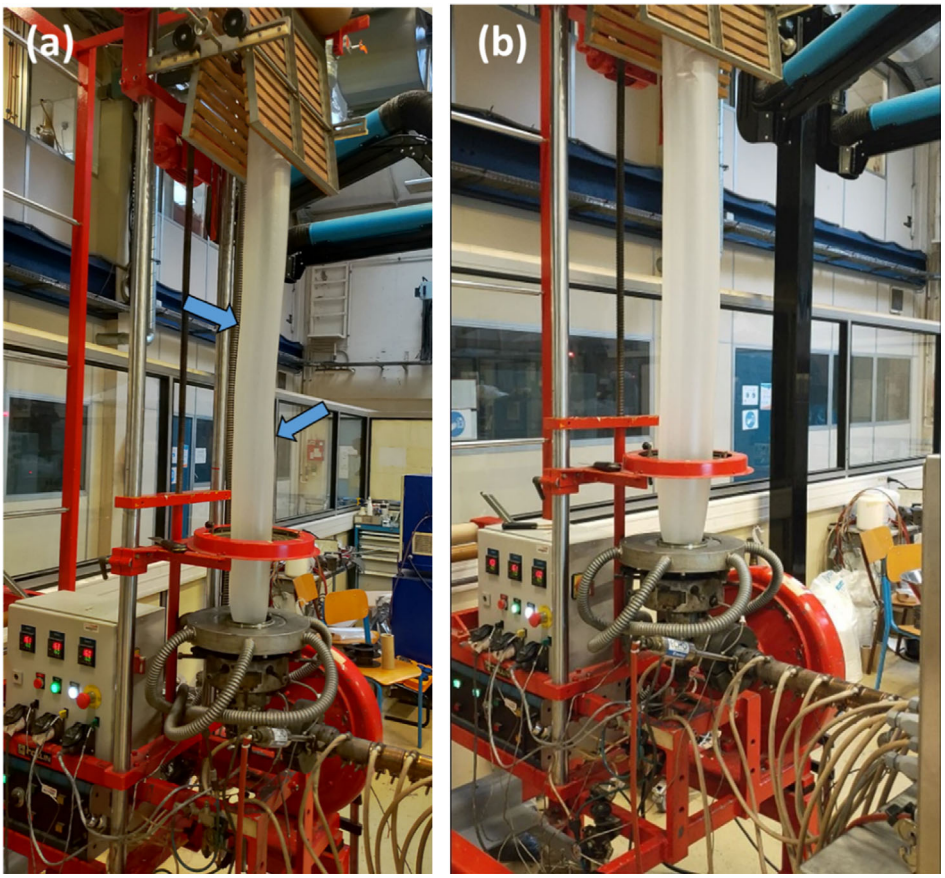

FIGURE 6 Film blowing of (a) unplasticized PHBV/PBSA 70/30/0.2Lp with BUR of 3.1 (arrows indicate instabilities) and (b) plasticized PHBV/PBSA/ATBC 63/27/10/0.2Lp with BUR of 3.9, height of the blow film bubble is about 180 cm. [Color figure can be viewed at wileyonlinelibrary.com]

blend produced a remarkably stable bubble without any sticking issues (Figure 6b). ATBC, in addition to its role as a plasticizer, acted as a processing aid by serving as a lubricating agent. Due to the limited solubility of ATBC in the blends, a portion of it likely migrated to the film's surface, where it functioned probably as a lubricant. This led to a favorable increase in the BUR to 3.9, subsequently reducing the DDR. Smaller DDR values are generally advantageous for bubble stability and mitigating draw resonance. Previous studies achieved a BUR of 2.5 for PHBV/PBAT blends[34] or between 1.8–2.1 using a coextrusion process for bi-layered PHB-PBAT films (PHB content ranging from 45 to 55%).[36] The formulation presented here exhibits substantial advancement for scaling up to an even larger production scale. This suggests its potential for the production of flexible film packaging based on commercially available PHBV.

3.4 | Testing of the performance of extrusion blown films in a food packaging application

3.4.1 | Food contact testing

The overall migration of substances from the extrusion blown films to food simulants was tested using the standard protocol of the European Regulation EU n°10/2011.

TABLE 8 Overall migration from PHBV/PBSA films into food simulants tested using the gravimetric method of the European Regulation EU n°10/2011.

	H_2O/ethanol 50/50 (v/v) (mg/dm^2)	Iso-octane (mg/dm^2)
PHBV	2.6 ± 0.3	3.3 ± 2.8
PBSA	4.4 ± 0.5	3.4 ± 1.2
PHBV/PBSA/DCP	4.0 ± 1.2	1.0 ± 0.7
PHBV/PBSA/0.2Lp	5.4 ± 1.2	3.8 ± 0.4
PHBV/PBSA/ATBC10/0.2Lp	41 ± 9	33 ± 16

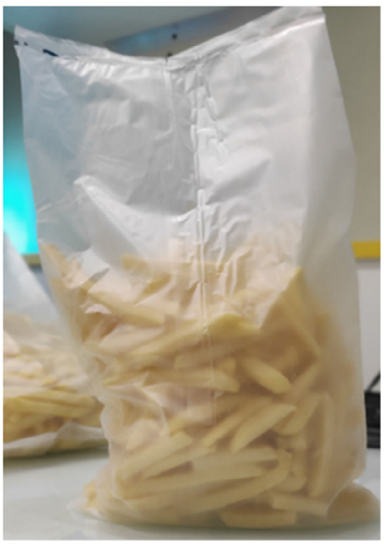

FIGURE 7 Hot sealed film of PHBV/PBSA/ATBC10/0.2Lp filled with 625 g of parfried frozen French fries. [Color figure can be viewed at wileyonlinelibrary.com]

It sets an overall migration limit of 10 mg/dm^2 of packaging (60 mg/kg food). If this limit is exceeded, the packaging does not comply with the EU safety standards. The test results of the films using simulants of fatty food and oily vegetable preparations are shown in Table 8. All formulations were compliant, except the formulation containing ATBC. Probably, ATBC was extracted during the migration. The quantity and the permanence of the plasticizer needs to be further optimized in the future.

The blends could be heat sealed using a vacuum packing machine. An image of a bag obtained with PHBV/PBSA/10ATBC/0.2Lp is shown in Figure 7. Flexible films are generally used for the packaging of frozen food, where they must perform in a large temperature range. We tested the stability of bags obtained from the film blowing extrusion by filling them with parfried French fries (Figure 7) and storing them for 3 months at – 20°C. Qualitatively, no evolution of the films was observed.

3.4.2 | Mechanical performance of extrusion blown films in service conditions

The thermal properties of the extrusion blown films are reported in Table 9. They were comparable to the properties obtained after the optimization of the blend composition with the batch mixer (Table 5). The PHBV/PBSA/ATBC10/0.2Lp blend had significantly higher crystallinity degree and lower T_g, most probably because of the higher mixing efficiency of the pilot scale process. The tensile properties of the extrusion blown films were evaluated in ambient and freezer temperature and after the aging test in food contact. The test of the impact strength was done on thermo-compressed samples with higher thickness fabricated using the twin-screw extruded pellets. Charpy unnotched impact tests (Table 9) showed improved toughness in the compatibilized blends with respect of pure PHBV (2.0 kJ.m^2, ref.).[44] The addition of ATBC increased the impact strength, showing the positive and synergistic action of the plasticizer together with the crosslinker and chain extender.

Tensile testing showed that the extrusion blown films without plasticizer were somewhat more rigid than that obtained by thermocompression during the formulation development. The film containing ATBC had but essentially the same properties (Table 5 versus Table 9). The maximum stress and the elongation at break of the PHBV/PBSA/DCP blends were not significantly different in machine and transverse direction. There was however a small, unexpected, increase in Young's modulus in transverse direction compared to machine direction. The blends incorporating Luperox® exhibited anisotropic characteristics between the machine and transverse directions, with all properties being notably superior in the machine direction. This outcome was expected, as the extrusion blowing fosters the preferential orientation of macromolecular chains due to shear stress in the die and stretching induced by pinch rolls during film blowing.[62] This phenomenon is consistent with prior observations in PHBV/PBAT blends.[34] Notably, the 4% elongation at break was achieved using ATBC. Although still modest, this property outperformed the enhancements reported in many other literature sources concerning plasticized PHBV or PHB[14,17,21,63,64] or stood on par with them.[12,15,19,20,24,65]

The mechanical properties at freezer condition showed, as expected, an increase of the elastic modulus and the maximum stress. Interestingly, the elongation at

TABLE 9 Thermal properties measured by DSC at the second heating scan (crystallinity degree) and the heating scan after physical aging of PHBV or PBSA (T_g), tensile properties and Charp unnotched impact strength of plasticized and unplasticized PHBV/PBSA/Luperox® blends in machine direction (MD) and transverse direction (TD) at ambient and freezer temperature.

	Thermal properties					Young modulus (MPa)		Maximum stress (MPa)	Elongation at break (%)			Impact strength (kJ.m−2)[c]
	PHBV		PBSA			Measurement T°						
	χ(%)	Tg (°C)	χ(%)	Tg (°C)		23°C	−20°C	23°C	−20°C	23°C	−20°C	23°C
PHBV/PBSA/DCP	59 ± 4	−1.5 ± 0.3	34 ± 11	−48.3 ± 0.2	MD	2308 ± 760[a]	n.d.	22 ± 4[a]	n.d.	1.3 ± 0.4[a]		2.8 ± 0.3[d]
					TD	2756 ± 251[b]		18 ± 6[a]		1.2 ± 0.3[a]		
PHBV/PBSA/0.2Lp	62 ± 1	−1.8 ± 0.1	32 ± 4	−47.8 ± 0.2	MD	2165 ± 96[a]	2408 ± 888	18 ± 2[a]	43 ± 6	1.8 ± 0.4[a]	1.6 ± 0.3	3.6 ± 0.5
					TD	2050 ± 140[b]	n.d.	11 ± 4	n.d.	0.7 ± 0.2[b]	n.d.	
PHBV/PBSA/ATBC10/0.2Lp	63 ± 2	−3.9 ± 0.3	40 ± 2	−53.2 ± 0.3	MD	1115 ± 94[a]	1774 ± 354[a]	14 ± 2[a]	37 ± 3[a]	4.2 ± 0.5[a]	4.8 ± 0.5[a]	7.7 ± 0.5
					TD	1064 ± 94[b]	1731 ± 412[a]	11 ± 2[b]	29 ± 3[b]	2.5 ± 0.7[b]	2.3 ± 0.4[b]	
	55	−2.3	37	−52.3	Aged	986 ± 145	n.d.	13 ± 3	n.d.	4.9 ± 0.9	n.d.	n.d

[a]Statistical different groups (MD vs TD) at $p < 0.05$.
[b]Statistical different groups (MD vs TD) at $p < 0.05$.
[c]Measured on samples obtained by thermo-compression of the twin-screw extruded pellets.
[d]Values reproduced from ref.[44] were obtained by twin screw extrusion followed by thermo- compression molding, Aged: 3 months at −20°C in contact with fatty food.

break did not change. Some results of tensile properties at low temperature are available in literature. PLA/PBAT 40/60 blends showed a change in fracture behavior from ductile to brittle at −25°C (220% to 20% elongation at break), because the T_g of PBAT was close to the freezer temperature.[66] Although the PHBV/PBSA blends had much lower elongation at break, the lower T_g of PBSA might help to stabilize the properties at freezer temperatures. The tensile properties of the films were stable during the aging test for 3 months in contact with food (Table 9). The thermal properties of the aged films in freezer conditions in contact with French fries showed lower crystallinity degree and higher T_g. Because we measured the properties after erasing the thermal history, the T_g increase could be caused by plasticizer exudation. The changes in crystallinity degree might be caused by some heterogeneity in the samples.

4 | CONCLUSION

New blends of PHBV/PBSA with a high concentration of PHBV (70 wt%) were developed. To increase the compatibility between both polymers, two organic peroxides were use as reactive compatibilizers, DCP and Luperox®. Luperox®, which is approved for food contact in contrary to DCP, was more efficient in inducing crosslinking reactions, as evidenced by the higher gel content. The analysis of the blend rheology with the van Gurp-Palmen plot evidenced the formation of long-chain branching, which was positive for the melt strength of the blends. The plasticizing of compatibilized PHBV/PBSA blends with ATBC decreased melt viscosity. It increased processability, notably in the extrusion blowing process. A stable bubble of 180 cm height was obtained. The highest BUR was reached with the blend PHBV/PBSA/ATBC10/0.2Lp. Impact strength and ductility could be increased using ATBC, improving the handling of the films in service situation although the elongation at break was still low. The properties of the films were stable during a 3 months aging test in food contact. However, the overall migration of films containing ATBC was higher than the regulatory limit. Further optimization must address this issue. In conclusion, PHBV-based blends were developed for flexible food packaging, which are able to be film blown thanks to the synergy of Luperox® and the plasticizer ATBC. The PHBV/PBSA/ATBC/Luperox® blend is a good candidate for scaling up the fabrication of in flexible films used in packaging.

AUTHOR CONTRIBUTIONS

Benjamin Le Delliou: Conceptualization (lead); data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); writing – original draft (lead). **Olivier Vitrac:** Conceptualization (equal); funding acquisition (lead); investigation (supporting); project administration (equal); supervision (equal); writing – review and editing (equal). **Anir Benihya:** Data curation (supporting); investigation (supporting); methodology (equal); writing – review and editing (supporting). **Alain Guinault:** Conceptualization (lead); formal analysis (lead); investigation (lead); methodology (lead); writing – review and editing (equal). **Sandra Domenek:** Conceptualization (lead); data curation (equal); formal analysis (lead); funding acquisition (lead); investigation (equal); methodology (equal); project administration (lead); writing – original draft (lead).

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DATA AVAILABILITY STATEMENT

Data will be made available upon request.

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REFERENCES

[1] D. Garcia-Garcia, L. Quiles-Carrillo, R. Balart, S. Torres-Giner, M. P. Arrieta, *Eur. Polym. J.* **2022**, *178*, 111505.
[2] S. K. Juikar, S. G. Warkar, *Packag. Technol. Sci.* **2023**, *36*, 229.
[3] B. Laycock, P. Halley, S. Pratt, A. Werker, P. Lant, *Prog. Polym. Sci.* **2014**, *39*, 397.
[4] A. El-Hadi, R. Schnabel, E. Straube, G. Mûller, S. Henning, *Polym. Test.* **2002**, *21*, 665.
[5] A. Ruellan, V. Ducruet, S. Domenek, in *Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications* (Eds: A. Jiménez, M. Peltzer, R. A. Ruseckaite), The Royal Society of Chemistry, London **2015**.
[6] G. Wypych, *Handbook of plasticizers*, 3rd ed., ChemTech Publishing, Toronto **2017**.
[7] A. K. Doolittle, *Technology of solvents and plasticizers*, John Wiley & Sons, New York **1954**.

[8] N. Varol, N. Delpouve, S. Araujo, S. Domenek, A. Guinault, R. Golovchak, A. Ingram, L. Delbreilh, E. Dargent, *Polymer* **2020**, *194*, 9.

[9] S. Araujo, N. Delpouve, S. Domenek, A. Guinault, R. Golovchak, R. Szatanik, A. Ingram, C. Fauchard, L. Delbreilh, E. Dargent, *Macromolecules* **2019**, *52*, 6107.

[10] M. Rapa, R. N. Darie-Nita, E. Grosu, E. E. Tanase, A. R. Trifoi, T. Pap, C. Vasile, *J. Optoelectron. Adv. Mater.* **2015**, *17*, 1778.

[11] D. G. Brunel, W. M. Pachekoski, C. Dalmolin, J. A. M. Agnelli, *Mater. Res.* **2014**, *17*, 1145.

[12] D. M. Panaitescu, C. A. Nicolae, A. N. Frone, I. Chiulan, P. O. Stanescu, C. Draghici, M. Iorga, M. Mihailescu, *J. Appl. Polym. Sci.* **2017**, 134. https://doi.org/10.1002/app.44810

[13] J. S. Choi, W. H. Park, *Polym. Test.* **2004**, *23*, 455.

[14] R. C. Baltieri, L. H. I. Mei, J. Bartoli, *Macromol. Symp.* **2003**, *197*, 33.

[15] L. Martino, M. A. Berthet, H. Angellier-Coussy, N. Gontard, *J. Appl. Polym. Sci.* **2015**, 132. https://doi.org/10.1002/app.41611

[16] D. F. Parra, J. Fusaro, F. Gaboardi, D. S. Rosa, *Polym. Degrad. Stab.* **1954**, *2006*, 91.

[17] R. Requena, A. Jiménez, M. Vargas, A. Chiralt, *Polym. Test.* **2016**, *56*, 45.

[18] I. T. Seoane, P. Cerrutti, A. Vazquez, V. P. Cyras, L. B. Manfredi, *Polym. Bull.* **2019**, *76*, 967.

[19] I. T. Seoane, L. B. Manfredi, V. P. Cyras, *J. Appl. Polym. Sci.* **2018**, *135*, 46016.

[20] J. L. Barbosa, G. B. Perin, M. I. Felisberti, *ACS Omega* **2021**, *6*, 3278.

[21] V. Jost, H.-C. Langowski, *Eur. Polym. J.* **2015**, *68*, 302.

[22] M. C. S. Corrêa, M. C. Branciforti, E. Pollet, J. A. M. Agnelli, P. A. d. P. . Nascente, L. Avérous, *J. Polym. Environ.* **2012**, *20*, 283.

[23] M. Erceg, T. Kovačić, I. Klarić, *Polym. Degrad. Stab.* **2005**, *90*, 313.

[24] L. Wang, W. Zhu, X. Wang, X. Chen, G.-Q. Chen, K. Xu, *J. Appl. Polym. Sci.* **2008**, *107*, 166.

[25] A. Ruellan, A. Guinault, C. Sollogoub, V. Ducruet, S. Domenek, J. Appl. Polym. Sci. Special Issue: Manufacturing of Advanced Biodegradable Polymeric Components, 42476, DOI: 10.1002/APP.42476. **2015**.

[26] M. P. Arrieta, M. D. Samper, J. López, A. Jiménez, *J. Polym. Environ.* **2014**, *22*, 460.

[27] M. Terada, R. H. Marchessault, *Int. J. Biol. Macromol.* **1999**, *25*, 207.

[28] R. Muthuraj, M. Misra, A. K. Mohanty, *J. Appl. Polym. Sci.* **2018**, *135*, 45726.

[29] M. P. Arrieta, E. Fortunati, F. Dominici, J. López, J. M. Kenny, *Carbohydr. Polym.* **2015**, *121*, 265.

[30] M. P. Arrieta, M. D. Samper, M. Aldas, J. López, *Materials* **2017**, *10*, 1008.

[31] N. Burgos, I. Armentano, E. Fortunati, F. Dominici, F. Luzi, S. Fiori, F. Cristofaro, L. Visai, A. Jiménez, J. M. Kenny, *Food Bioprocess Technol.* **2017**, *10*, 770.

[32] M. Boufarguine, A. Guinault, G. Miquelard-Garnier, C. Sollogoub, *Macromol. Mater. Eng.* **2013**, *298*, 1065.

[33] T. Gerard, T. Budtova, A. Podshivalov, S. Bronnikov, *Express Polym. Lett.* **2014**, *8*, 609.

[34] M. Cunha, B. Fernandes, J. A. Covas, A. A. Vicente, L. Hilliou, *J. Appl. Polym. Sci.* **2016**, 133. https://doi.org/10.1002/app.42165

[35] L. Quiles-Carrillo, N. Montanes, J. M. Lagaron, R. Balart, S. Torres-Giner, *J. Polym. Environ.* **2019**, *27*, 84.

[36] P. F. Teixeira, J. A. Covas, M. J. Suarez, I. Angulo, L. Hilliou, *Int. Polym. Process.* **2020**, *35*, 440.

[37] J. H. Wang, Y. C. Tian, B. Zhou, *J. Polym. Environ.* **2022**, *30*, 1366.

[38] P. Ma, X. Cai, Y. Zhang, S. Wang, W. Dong, M. Chen, P. Lemstra, *Polym. Degrad. Stab.* **2014**, *102*, 145.

[39] P. Ma, D. G. Hristova-Bogaerds, P. J. Lemstra, Y. Zhang, S. Wang, *Macromol. Mater. Eng.* **2012**, *297*, 402.

[40] Z. B. Qiu, T. Ikehara, T. Nishi, *Polymer* **2003**, *44*, 7519.

[41] B. Palai, S. Mohanty, S. K. Nayak, *Polym. Test.* **2020**, *83*, 16.

[42] B. Le Delliou, O. Vitrac, M. Castro, S. Bruzaud, S. Domenek, *J. Appl. Polym. Sci.* **2022**, *139*, 52124.

[43] M. Zhang, N. L. Thomas, *Adv. Polym. Technol.* **2011**, *30*, 67.

[44] B. Le Delliou, O. Vitrac, A. Benihya, P. Dole, S. Domenek, *Polym. Test.* **2023**, *124*, 108072.

[45] P. J. Jandas, S. Mohanty, S. K. Nayak, *Ind. Eng. Chem. Res.* **2013**, *52*, 17714.

[46] A. R. Kolahchi, M. Kontopoulou, *Polym. Degrad. Stab.* **2015**, *121*, 222.

[47] W. Dong, P. Ma, S. Wang, M. Chen, X. Cai, Y. Zhang, *Polym. Degrad. Stab.* **2013**, *98*, 1549.

[48] K. Zhang, M. Misra, A. K. Mohanty, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2345.

[49] M. Carvalheira, L. Hilliou, C. S. S. Oliveira, E. C. Guarda, M. A. M. Reis, *Curr. Res. Biotechnol.* **2022**, *4*, 211.

[50] S. L. Sun, P. F. Liu, N. Ji, H. X. Hou, H. Z. Dong, *Food Hydrocolloids* **2017**, *72*, 81.

[51] M. Cunha, M. A. Berthet, R. Pereira, J. A. Covas, A. A. Vicente, L. Hilliou, *Polym. Compos.* **2015**, *1859*, 36.

[52] Y.-M. Corre, S. Bruzaud, J.-L. Audic, Y. Grohens, *Polym. Test.* **2012**, *31*, 226.

[53] S. Charlon, N. Follain, E. Dargent, J. Soulestin, M. Sclavons, S.-P. Marais, *J. Phys. Chem. C* **2016**, *120*, 13234.

[54] K. Iggui, M. Kaci, M. Mahlous, N. L. Moigne, A. Bergeret, *J. Renew. Mater.* **2019**, *7*, 807.

[55] M. Kunioka, Y. Doi, *Macromolecules* **1933**, *1990*, 23.

[56] P. Barham, A. Keller, *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 69.

[57] M. M. Quispe, O. V. Lopez, D. A. Boina, J. F. Stumbe, M. A. Villar, *Polym. Test.* **2021**, *93*, 107005.

[58] R. T. Umemura, M. I. Felisberti, *J. Appl. Polym. Sci.* **2021**, *138*, 49990.

[59] J. Tian, W. Yu, C. Zhou, *Polymer* **2006**, *47*, 7962.

[60] P. Zytner, F. Wu, M. Misra, A. K. Mohanty, *ACS Omega* **2020**, *5*, 14900.

[61] S. Trinkle, P. Walter, C. Friedrich, *Rheol. Acta* **2002**, *41*, 103.

[62] X. Zhang, S. Elkoun, A. Ajji, M. Huneault, *Polymer* **2004**, *45*, 217.

[63] E. J. Quirijns, A. J. B. Van Boxtel, W. K. P. Van Loon, G. Van Straten, *J. Sci. Food Agric.* **2005**, *1805*, 85.

[64] C. S. Reddy, K. O' Connor, R. Babu P, *Macromol. Symp.* **2016**, *365*, 223.

[65] R. R. De Sousa, C. A. S. Dos Santos, N. M. Ito, A. N. Suqueira, M. Lackner, D. J. Dos Santos, *Polymer* **2022**, *14*, 14.

[66] A. Pietrosanto, P. Scarfato, L. Di Maio, M. R. Nobile, L. Incarnato, *Polymer* **2020**, *12*, 804.

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