Combined compatibilization and plasticization effect of low molecular weight poly(lactic acid) in poly(lactic acid)/ poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) blends

A. Amor, N. Okhay, A. Guinault, G. Miquelard-Garnier, C. Sollogoub, M. Gervais[*]

PIMM–UMR 8006, ENSAM, CNRS, CNAM, 151 bvd. de l'Hôpital, 75013 Paris, France

Abstract. Improving overall properties of poly(lactic acid) (PLA) by blending it with another biobased polymer has been a strong field of research over the last years. In this study we demonstrate the synergetic effect of a small amount (between 0.1 and 1 wt%) of oligomer-like PLA (oLA) on the thermal, mechanical and gas barrier properties of the widely studied PLA-poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) blends (90–10 wt%). Films of PLA/PHBV/oLA blends were prepared via single-screw extrusion. oLA being miscible with both PLA and PHBV, its compatibilizing effect was demonstrated by a decrease of the interfacial tension, a slight shift in the T_gs of both polymers, and an increase in the elongation at break. It was also showed that oLA had a plasticizing effect on the PHBV dispersed phase, increasing its crystallinity rate. This resulted in a decrease in the permeability of the films while improving Young's modulus.

Keywords: *polymer blends and alloys, biopolymers, toughening, compatibilization, barrier properties*

1. Introduction

Biopolymers have received great attention both in industry and in academia due to an increased concern toward the environmental impact of plastic waste and the saving of limited fossil energy. Poly (lactide) (PLA), one of the most used biobased and biodegradable polymers, is synthesized from lactic acid obtained from renewable resources (corn, sugar, potato). Its properties make it a potential candidate to be used in various applications, such as packaging, medicine, agriculture, textile, and automotive industries [1]. However, despite its good optical properties and high tensile strength, its inherent brittleness and high gas permeability significantly limit its applications, especially in food packaging [1–4]. Many strategies have been recently developed and proposed to improve these properties, such as the addition of modifiers, copolymerization or blending [5–8].

Blending PLA with another biobased and biodegradable polymer has attracted much attention since it offers simply the opportunity to widen the range of physical properties, without compromising environmental features of the final material. Among polyhydroxyalcanoates (PHAs), which are aliphatic polyesters obtained by microbial fermentation, poly(3-hydroxybutyrate) (PHB) and its copolymers (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly (3-hydroxybutyrate-*co*-3-hydroxyoctanoate (PHBHO), poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx)…) have been largely used for PLA-based blends [9]. Some of the resulting blends exhibit improved properties compared to neat PLA: higher toughness and increased elongation at break [10–16], improved gas barrier properties [17, 18], increased thermal stability [16], enhanced biodegradability [14].

[*]Corresponding author, e-mail: matthieu.gervais@lecnam.net

Those improvements are partly due to the fact that, although immiscible, the two polymers have a certain degree of chemical affinity. Miscibility and compatibility of PLA/PHB(V) have been thoroughly studied and have been found to depend classically on the molecular weight of both components, the blending method, the blend composition and the crystallinity of both components. Blümm and Owen [19] observed miscibility of low molecular weight poly(L-lactide) (PLLA) ($\overline{M}_n$ = 1800 g/mol) and immiscibility of high molecular weight PLLA ($\overline{M}_n$ = 160 000 g/mol) blended with PHB ($\overline{M}_n$ = 222 000 g/mol) over the whole composition range. Similarly, Koyama and Doi [20] investigated the miscibility of PHB ($\overline{M}_w$ = 650 000 g/mol) blended with PLA of various molecular weights and determined that the blend is immiscible above a critical value of molecular weight of PLA around 20 000 g/mol. More generally, all literature agrees on the immiscibility of the blend as soon as the molecular weight of both components is high. Zhang *et al*. [21] found that melt blended samples exhibited greater compatibility than those prepared by solvent casting at room temperature, possibly due to a transesterification reaction between PHB and PLA occurring at high temperature. This transesterification, or more generally the presence of specific interactions between the two polymers, has been evidenced by many other authors [14, 15, 22–24], especially for blends containing a low amount of PHB(V). For such PLA/PHBV blends (typically weight fractions of 90%/10%), Gerard and Budtova [22] observed a peculiar morphology, with very small PHBV nodules (about 400 nm) well dispersed in PLA matrix, with increased adhesion at the interface, presumably explaining the increase of ductility (elongation at break of 200% when tested immediately after sample preparation) measured for this composition by the authors.

All those studies have highlighted the importance of the interface on the final properties of PLA/PHB(V) blends and some attempts have been undertaken to modify it, using different strategies. Yoon *et al*. [25] compatibilized a mixture of PHB and PLA ($\overline{M}_n$ = 56 000 g/mol) using synthesized Poly(ethylene glycol) – *b* – PLLA (PEG-*b*-PLLA) (PEG is known to be compatible with PHB) and poly(vinyl acetate) (PVAc, compatible with both PLA and PHB). A small improvement in toughness was obtained with the addition of 2 wt% of block copolymers or PVAc, but the overall mechanical properties were not improved much. One possible reason proposed by the authors could be the solubilization of the compatibilizer molecules in either PHB or PLA, or in both, instead of placing themselves at the interface between the PHB and PLA. Recently, an alternative approach was proposed by Yang *et al*. [26] by adding transesterification catalysts in order to induce chemical reaction between the two components. They found a significant effect on the mechanical properties by adding a small amount of zinc acetate (0.1 wt% in the blend).

Finally, some authors have formulated PLA/PHB(V) blends in order to improve their mechanical properties and/or processability, adding different components as plasticizers, either commercial or synthesized ad-hoc: PEG [27, 28], ATBC [28], limonene [29], polyester plasticizer (Lapol 108) [30], lactic acid oligomer (oLA) [31] and tributyrin [32]. It has been accepted that concentrations from 10 to 20 wt% and up to 30 wt% are required to provide a substantial plasticization effect, which strongly modifies the mechanical properties: if the ductility is usually enhanced, the Young's modulus and the tensile strength are decreased. Besides, the gas barrier properties of the plasticized blends are often deteriorated as a consequence of the incorporation of the plasticizer, which induces a gain of mobility of the polymer chains. Nevertheless, some authors noticed that, when the plasticizer has good miscibility with both of the components, it can have a beneficial effect on the compatibility between them. For instance, Armentano *et al*. [31] observed a reduction of the size of PHB domains with the addition of oLA ($\overline{M}_n$ = 957 g/mol) in PLA/PHB (85/15 wt%), indicating improved interfacial properties. The enhanced ductility can therefore be interpreted as the consequence of a combined effect of plasticization and compatibilization. This oLA was added from 15 to 30 wt%.

In this study, we develop a different strategy to compatibilize PLA/PHBV blends, while preserving their tensile strength, gas barrier properties and bio-based character. It consists in introducing a much smaller amount (between 0.1 and 1 wt%) of hydrolyzed PLA having an oligomer-type molar mass ($\overline{M}_n$ = 5 000 g/mol) to the PLA/PHBV blends. It is anticipated that the low molecular weight PLA (oLA) will improve the compatibility between PLA and PHBV without a significant drop in the mechanical properties. The resulting thermal, morphological, mechanical and gas barrier properties of the obtained bio-based PLA/PHBV blends are investigated.

2. Experimental part

2.1. Materials

2003D PLA, an extrusion grade, was purchased from Natureworks, USA. This PLA is a Poly(D,L-lactide) with a percentage of D-lactic acid units of 4.3% [33]. Its melt temperature is close to 152 °C with a melt flow index of 6 g/10 min (210 °C, 2.16 kg) as given by Natureworks. The molecular weight as determined by SEC is $\overline{M}_w \approx 150\,000$ g/mol with a dispersity $Đ$ of 2.5. SEC was performed at 40 °C using THF (GPR Rectapur, VWR, France) as eluant on a Waters apparatus (USA) equipped with three columns Styragel HR0.5, HR3 and HR4 and with a Waters 2414 refractive index detector at an elution rate of 1 mL/min. Polystyrenes were used as standards.

ENMAT Y1000P Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) PHBV was obtained from Tianan Biologic, China. Y1000P is an additivated PHBV containing 8 mol% of HV groups, and $\overline{M}_w \approx 340\,000$ g/mol ($Đ \approx 2.5$) [34], with a melt temperature close to 170 °C. The melt flow index is reported to be 2.4 g/10 min at 170 °C (2.16 kg) [35]. The chemical structure of the two polymers is shown Figure 1.

2.2. Synthesis of low molecular weight PLA

Low molecular weight PLA <20 000 g/mol is known to be miscible with PHB [19, 20]. The low molecular weight PLA (5000 g/mol) that will be added to PLA/PHBV is obtained by the hydrolysis of 2003D PLA. PLA has indeed the advantage of being highly hydrolysable. This hydrolysis can be accelerated by many factors, such as temperature and pH of the reaction mixture [36].

The hydrolysis is realized in distilled water at neutral pH and at a temperature of 100 °C. About 40 g of PLA are introduced into 4 L of water in a mount of reflux containing a round-bottom flask of 5 L. The use of a large amount of water will keep a pH close to 7 during degradation. Indeed the production of lactic acid during the degradation tends to acidify and catalyze the hydrolysis reaction which may cause a rapid degradation of the macromolecular chain or a change in the degradation mechanism.

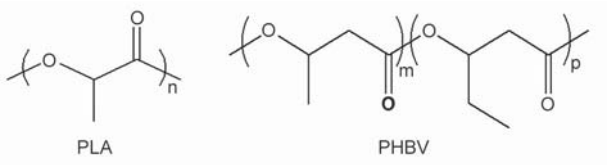

Figure 1. Chemical structure of PLA and PHBV

The obtained samples are dried to a constant weight in a ventilated oven at 65 °C and their molecular weight is measured by size-exclusion chromatography (SEC) using the same protocol as previously described.

SEC analyses of the PLA after 2 to 43 hours of hydrolysis have two molecular chains distributions (one around 5000 g/mol and one with a higher average molar mass). After 45 hours, a single distribution around 5000 g/mol is obtained. Therefore the oLA ($\overline{M}_n \approx 5000$ g/mol) with $Đ$ close to 1.25 is selected for this study.

2.3. Film samples preparations

PHBV and PLA were used as received, in pellet form, but dried with desiccant air before use (4 h at 90 °C for the PHBV, 4 h at 80 °C for the PLA). PLA, PHBV and oLA pellets were then dry-blended in proportions of (90 – *x*) wt%, 10 wt% and *x* wt% (with *x* = 0, 0.1, 0.5 or 1) respectively and then extruded in a single-screw extruder SCAMEX Rheoscam (France) (with a screw diameter of 20 mm and a length over diameter of 20, a screw speed of 60 rpm, and an operation temperature of 175–185 °C). A flat die allowed obtaining films (thickness of 0.35 mm and width of 100 mm). The final composition of the blend will be given in PLA/ PHBV/oLA form in the following.

PHBV and PLA additivated with oLA were also realized for some experiments using the following solvent cast procedure: oLA was introduced in PHBV (or PLA) dissolved in chloroform (GPR Rectapur, VWR, France) with different ratios (0, 1, 5 and 10 wt%) at 55 °C. The obtained solution was then transferred into aluminum pans which were placed in a vacuum oven at 65 °C to obtain films by solvent evaporation. Those blends will be referred as PHBV or PLA (solvent cast) and PHBV (or PLA)/oLA *y* wt% with *y* = 1, 5 and 10.

2.4. Determination of interfacial tension

A relevant parameter to discuss the compatibility of polymer blends is the interfacial tension between two polymers. To determine the interfacial tension, several methods can be used [37], among which the relaxation drop method was chosen. A Linkam optical rheology system (UK) was used for shearing polymers under an optical microscope equipped with a camera. A small quantity of PHBV was placed between two PLA sheets and sheared until individual PHBV droplets can be isolated under the microscope

at 185 °C. Then, a small shear rate was applied for a very short time on the sample: the droplet deforms into an ellipsoid. When shear is stopped, the droplet relaxes back to its initial spheroidal shape. The evolution of the long axis of the ellipsoid as a function of time follows an exponential decay with a characteristic relaxation time related to the viscosity ratio of the polymers and the interfacial tension following Equation (1):

$$\tau_d = \frac{\eta_m r_0}{\gamma_{12}} \cdot \frac{(19K+16)(2K+3)}{40(K+1)} \quad (1)$$

where τ_d is the relaxation time due to the relaxation of the interface, η_m is the viscosity of the matrix, γ_{12} is the interfacial tension of the blend, r_0 is the mean radius of the drop, and $K = \eta_d/\eta_m$ is the zero shear viscosity ratio of the droplet and matrix. The shear viscosity was deduced from dynamic shear measurements carried out at 185 °C on an Anton Paar MCR 502 rheometer using 25 mm diameter parallel plates (1 mm gap) under a shear strain of 1%.

For assessing reproducibility, measurements were carried out on at least five different samples. In order to see the effect of oLA on the PLA/PHBV interfacial tension, the same measurement had been performed with PHBV additivated with oLA realized by solvent cast (see details above).

2.5. Samples characterization

2.5.1. Differential scanning calorimetry (DSC) measurements

Glass transition temperatures and melting enthalpies of the polymer samples were measured using a TA Instruments Q10 machine (USA), which was equipped with a DSC Refrigerated Cooling System to achieve low temperatures. Polymer samples were weighed (5 to 10 mg) and placed into non-hermetic aluminum pans individually. DSC analysis was done under nitrogen (50 mL/min) by first heating the sample to 200 °C at 10 °C·min^{-1} to erase its thermal history, then equilibrating the samples at –20 C, followed by ramping up the temperature to 200 °C at a rate of 10 °C per minute. The crystallinity ratio of the polymers χ_c was calculated by Equation (2):

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{w \Delta H_m^0} \cdot 100 \quad (2)$$

where χ_c [%] is the crystallinity ratio, ΔH_m [J·g^{-1}] the melting enthalpy, ΔH_{cc} [J·g^{-1}] the cold crystallization enthalpy, w the weight fraction of the polymer in the blend and ΔH_m^0 the melting enthalpy of a 100% crystalline polymer, reported to be 93 J·g^{-1} for PLA [38] and 109 J·g^{-1} for PHBV [39].

2.5.2. Dynamic mechanical thermal analysis (DMTA) experiments

The thermo-mechanical behavior has been investigated using a dynamic thermomechanical analyzer DMTA from BOHLIN INSTRUMENTS (UK). A temperature scan from –40 up to 200 °C was performed at the rate of 2 °C·min^{-1} while a dynamic tensile test was performed at a frequency of 1 Hz with a deformation of 0.5%.

2.5.3. Tensile tests

Films mechanical properties (Young's modulus E, tensile strength σ_y and elongation at break ε_b) were measured on an Instron 4507 (UK) with a 100 N load cell with no extensometer. At least five dog-bone shaped samples, with 58 mm of length and 5 mm in width, were taken in the center of the film in the extrusion direction. The deformation rate was fixed at 5 mm·min^{-1} for all samples, force and deformation were measured and stresses and strains were calculated from these measurements. For each sample, average values of elongation at break and Young's modulus (calculated by taking the initial slope of the stress–strain curves) were collected and compared.

3.5.4. Atomic force microscopy (AFM) studies

The morphology and the size of the dispersed phase in the polymer blends were investigated via AFM. Samples were sectioned in the cross section of the film with an ultramicrotome 2088 UltrotomeV (LKB, Sweden) at a cutting speed of 1 mm/s.

A VEECO, MultiMode Nanoscope-model V (2008) AFM (USA) working in Tapping mode, in air using silicon nitride tips was used in this study. Images were recorded using scan speeds on the order of 10 mm/s and the applied force was the minimum possible (~1 nN). The obtained images were processed by ImageJ software to determine the area, width and length of PHBV (or additivated PHBV) nodules within the PLA matrix. 5 images for each of two blends PLA/PHBV and PLA/PHBV/oLA 1 wt%, were analyzed, corresponding to a number of nodules higher than 100 (147 and 111 respectively).

2.5.5. Gas permeability

Helium permeability was measured by a specific homemade analyzer at 23 °C and 0% relative humidity, based on the ISO 15105-2:2003 method. Circular portions cut from the films (surface = 23.75 cm^2) were inserted between two hermetically sealed compartments drained using nitrogen. A helium constant flow (80 $mL \cdot min^{-1}$) was introduced in the downstream part of the cell and is measured in the upstream part, using an helium detector (mass spectrometer).

Measuring helium permeability rather than oxygen permeability presents several advantages: because helium molecules are smaller than oxygen, experimental time is reduced from 24 hours to 30 min. Moreover, helium is a neutral gas, which prevents from any possible interaction of the permeant gas within the polymer matrix and appears thus as a relevant probe of the blend morphology. Permeability was determined from the transmission rate. For assessing reproducibility of permeability, measurements were carried out on at least two different samples obtained from the same film.

3. Results and discussion

3.1. Characterization of PHBV and PLA additivated with oLA (obtained by solvent casting)

Differential scanning calorimetry (DSC) analysis of different additivated PHBV and PLA formulations was conducted in order to determine the effect of the PLA short chains introduction on the thermal properties of PHBV and PLA. DSC thermal properties of the neat PHBV, PLA, oLA and of different PHBV/oLA and PLA/oLA formulations are summarized in Table 1. Note that the ratio of oLA compared to PHBV in the formulations here is the same as in the final PLA/PHBV/oLA blends. Only the second heating has been considered for a better comparison with what happened after single screw extrusion.

The T_g value for neat PLA during the first and second heating scan is about 60 °C. However the thermogram of neat PHBV does not show any T_g peak. Indeed DSC is not sensitive enough for the detection of this T_g, given the high crystallinity of PHBV. From melting enthalpy, the degree of crystallinity of the different formulations can be determined. oLA has, as expected, a lower T_g compared to PLA as well as a lower T_{cc} and T_m and a higher crystallinity ratio.

Addition of oLA to PLA from 1 to 5 wt% does not influence the T_g of PLA nor the degree of crystallinity. Therefore the addition of oLA by itself in PLA does not induce any modification of the behavior of PLA with the amount added to the system. oLA is not expected to have any influence in PLA/PHBV/oLA blends on the PLA part as the amount used will be lower or equal to 1 wt%.

PHBV crystallinity ratio is evolving with the process used. Solvent casting the polymer tends to increase its crystallinity. The degrees of crystallinity, calculated with a ΔH_m^0 value of 109 J/g for 100% crystalline PHBV, are extremely high. That may be due to an underestimated ΔH_m^0 value considering the fact that other higher values are reported in literature (164 J/g [40], 146 J/g [41, 42]). A slight decrease is observed when oLA is added to PHBV. 5 wt% leads to the highest value of crystallinity ratio for the PHBV/oLA formulations

3.2. Interfacial tension between PLA and additivated PHBV

The interfacial tension between PLA and PHBV additivated with different concentrations of oLA have

Table 1. Thermal analysis properties of PLA, PHBV, PLA/oLA and PHBV/oLA blends (all obtained by solvent cast) as a function of the amount of oLA [wt%] (2nd heating run)

	T_g [°C]	T_m PLA [°C]	T_m PHBV [°C]	T_{cc} [°C]	ΔH_{cc} [J/g]	ΔH_m [J/g]	χ_c (PHBV) [%]	χ_c (PLA) [%]
PLA (solvent cast)	60	151	–	121	22.6	23.70	–	1.0
PLA (pellet)	61	153	–	–	5.0	6.10	–	1.0
PHBV (solvent cast)	–	–	172	–	–	100.80	92.5	–
PHBV (pellet)	–	–	173		–	92.50	85.0	–
oLA (pellet)	43	143	–	94	42.1	59.60	–	18.0
PHBV/oLA 99/1	–	–	172	–	–	78.60	73.0	–
PHBV/oLA 95/5	–	–	167	–	–	86.40	83.0	–
PHBV/oLA 90/10	–	–	169	–	–	76.80	70.0	–
PLA/oLA 99/1	60	150	–	116	23.2	28.20	–	1.5
PLA/oLA 95/5	59	150	–	115	26.6	26.95	–	0.2

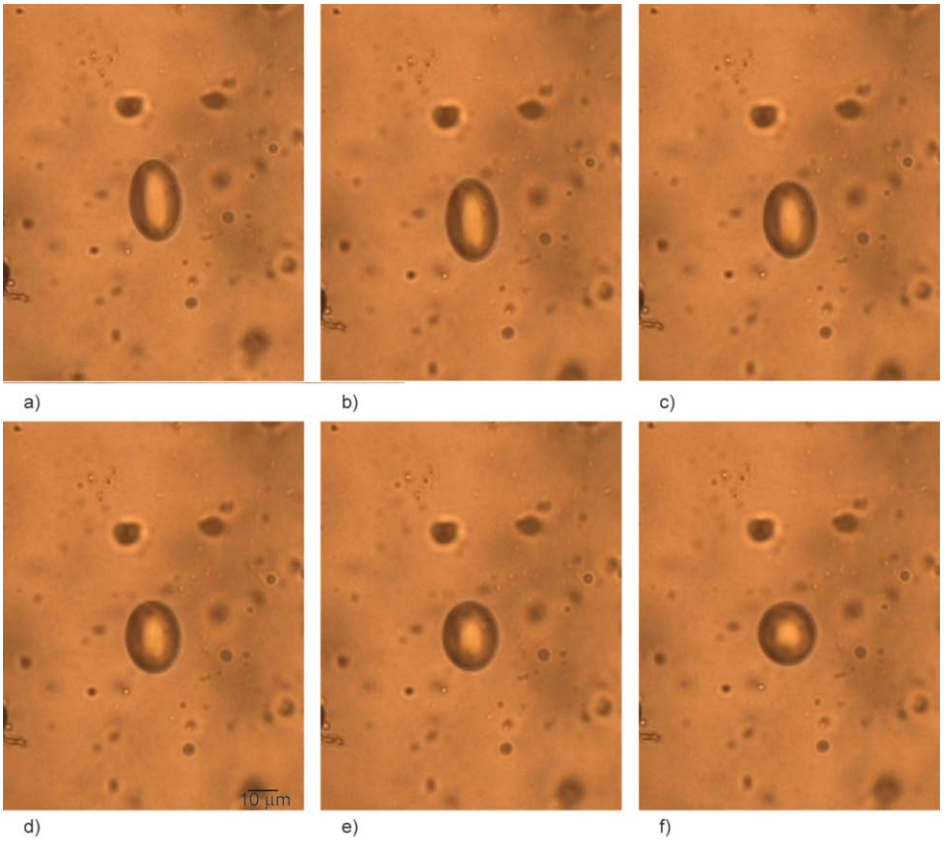

Figure 2. PHBV drop relaxation in PLA matrix, a) 0 s, b) 8 s, c) 16 s, d) 24 s, e) 30 s, f) 60 s

been measured via the relaxation drop method. A typical drop relaxation of PHBV dispersed in a PLA matrix is shown in Figure 2 and the relaxation time from the ellipsoid shape after shear to circular has been used to estimate the interfacial tension for each blend using Equation (1). The results have been summarized in Table 2. From the results, a few remarks can be made. First of all, a decrease of the interfacial tension between PLA and PHBV after addition of the oLA is observed, revealing the compatibilizing effect of the oLA. In fact, when oLA (1 wt% in the PHBV phase) is added to the blend, the interfacial tension decreases from 0.5 to 0.3 mN/m, as presented in Table 2. From 1 to 10 wt% of oLA in PHBV, the interfacial tension remains almost unchanged. This phenomenon can be explained by the fact that the interface may be already saturated with 1 wt% of oLA.

Table 2. tension of PLA/PHBV blends as a function of the amount of PLA short chains added in the PHBV [wt%]

	Viscosity ratio at 185°C (η_{PLA} = 4800 Pa·s)	**Interfacial tension [mN/m]**
PHBV/PLA	0.27	0.50±0.08
[PHBV/oLA (99/1)]/PLA	0.21	0.31±0.01
[PHBV(oLA (95/5)]/PLA	0.13	0.33±0.05
[PHBV/oLA (90/10)]/PLA	0.13	0.36±0.02

3.3. Films characterization

3.3.1. Thermal analysis

The DSC thermograms from the first heating run of neat PLA, PHBV, PLA/PHBV and PLA/PHBV/oLA films realized by single-screw extrusion are shown in Figure 3. The curves reveal different thermal events as follows: the glass transition (T_g), the cold-crystallization (characterized by T_{cc} and the enthalpy of crystallization ΔH_{cc}), the melting point (characterized by

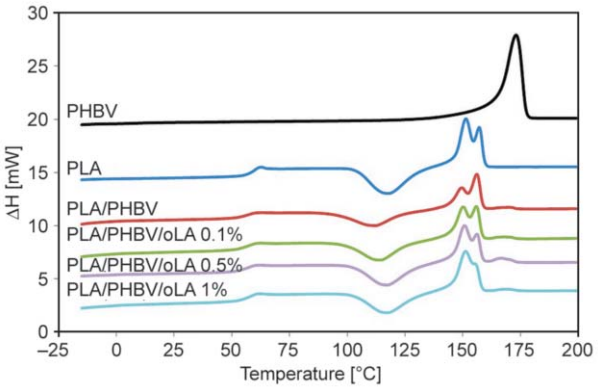

Figure 3. First heating run in DSC for PLA, PLA/PHBV and PLA/PHBV/oLA films and PHBV pellets

Table 3. Thermal analysis of PLA, PLA/PHBV and PLA/PHBV/oLA films as a function of the amount of oLA [wt%]

		T_g [°C]	T_{m1} [°C]	T_{m2} [°C]	T_{m3} [°C]	T_{cc} [°C]	ΔH_{m3} (PHBV) [J/g]	ΔH_{cc} [J/g]	χ_c (PLA) [%]	χ_c (PHBV) [%]
2nd heating run	PLA	60	151	157	–	118	–	34	0.1	–
	PLA/PHBV	57	150	156	169	111	1.96	29	3.2	18
	PLA/PHBV/oLA 0.1%	57	150	156	167	114	1.76	29	1.4	16
	PLA/PHBV/oLA 0.5%	57	151	156	167	117	3.38	31	0.6	31
	PLA/PHBV/oLA 1%	58	151	–	168	117	1.47	31	0.0	13
1st heating run	PLA	58	152	157	–	119	–	34	1.1	–
	PLA/PHBV	56	147	156	170	105	5.53	29	2.7	51
	PLA/PHBV/oLA 0.1%	55	147	156	170	104	5.54	29	1.5	51
	PLA/PHBV/oLA 0.5%	55	148	156	170	105	8.08	28	1.2	74
	PLA/PHBV/oLA 1%	54	148	156	171	105	5.92	26	0.6	54

T_m and the melting enthalpy ΔH_m). All these data are summarized in Table 3.

The T_g value for the PLA neat film was about 60 °C, while the exothermic peak is observed at about 118 °C and the multi-step melting endothermic peak is obtained at about 151–157 °C. The DSC thermograms for the PLA/PHBV blend display a slight shift to lower T_g values with respect to neat PLA and a similar multi-step melting with the first and second peaks (T_{m1} and T_{m2}) due to the PLA and the third one (T_{m3}) corresponding to the PHBV around 170 °C. This suggests no complete miscibility between the two polymers [43].

The double melting peak in the range of 147–156 °C can be attributed to the formation of different crystal structures for the PLA [16, 44].

In the first heating run, characterizing the thermal properties of the films 'as prepared', a slight decrease of the glass transition temperature of PLA from 58 °C for the neat PLA film to 56 °C for the PLA/PHBV film and 54 °C for the PLA/PHBV/oLA 89/10/1 is observed. This gradual decrease of the T_g of PLA phase can be understood as an increase of compatibility of PLA/PHBV blends due to the presence of the oLA, miscible with both PLA and PHBV.

The cold crystallization temperature of PLA is decreased from 119 to 105 °C with the addition of PHBV, as already observed by previous authors [15, 16, 45], and is not influenced by oLA addition. The PLA degree of crystallinity also remains extremely low in every case (<5%).

When blended with high molar mass PLA, PHBV loses its crystallinity, with a sharp decrease from 85 to 51%, as confirmed by Ma *et al*. [11]. But the degree of crystallinity of PHBV increases when an optimum value of oLA is added (from 51% without any oLA to 74 with 0.5 wt% oLA). This follows the same trend as what has been observed for PHBV/oLA blends, with a maximum of crystallinity for 0.5 wt% oLA and can be seen as a plasticizing effect of the oLA on the dispersed PHBV phase. This effect may then hinder the crystallization at higher oLA amount (1 wt%). Such effect is also observed in the second heating run with an increase from 18 to 31% in the PHBV degree of crystallinity with 0.5 wt% of oLA compared to pure PHBV.

Finally, it can be noted that PHBV and oLA seems to have an impact on the crystalline forms of PLA. PHBV almost prevents the appearance of the crystalline form that melts at 150 °C while the addition of oLA has the opposite effect. With 1% of oLA, the 150 °C form is even predominant and in higher concentration than in PLA alone.

3.3.2. Morphology

Figure 4 shows the AFM micrographs of the fracture surface of PLA/PHBV (Figure 4a) and PLA/PHBV/oLA blends (Figure 4b). AFM images of PLA/PHBV films underlined that the dispersed PHBV phase had relatively small average diameter with a typical nodular morphology dispersed in the PLA polymer matrix. With the addition of 1 wt% of oLA, the size of the PHBV domains is reduced but the shape remains unchanged. The mean area goes from 0.14 μm^2 for the PLA/PHBV film to 0.11 μm^2 for the PLA/PHBV/oLA 89/10/1 film (Table 4) while the ratio length/width is around 2 in both cases. To support this observation and explain the standard deviation of the domains area measured for PLA/PHBV/oLA 1 wt%, the global distribution of the nodules sizes of PHBV is presented in Figure 5. If the PLA/PHBV film presents a broad single distribution, the additivated film shows a double distribution, with a sharper main distribution shifted to smaller size and the

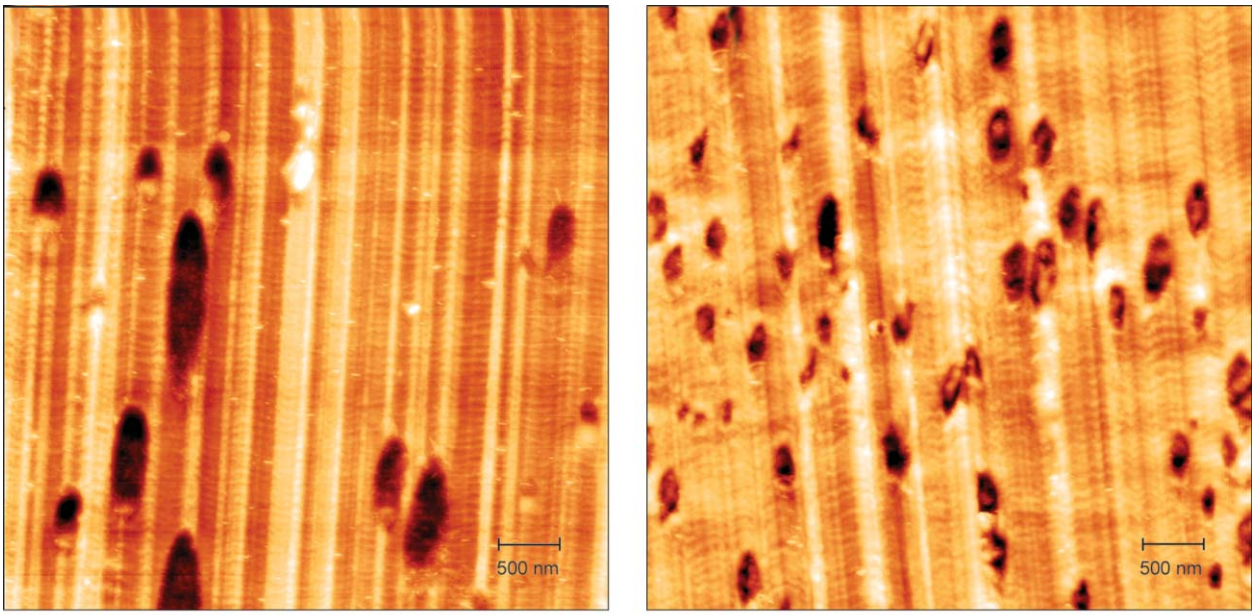

Figure 4. AFM micrographs of PLA/PHBV (90/10) (a) and PLA/PHBV/oLA (89/10/1) (b)

presence of a small portion of remaining large domains of PHBV (>0.4 μm^2) that increase the average size of the nodule observed. However a clear tendency to the decrease of PHBV size domain is observed: excluding the few remaining large domains, the average area of the compatibilized nodules is less than 0.09 μm^2 (while it is 0.13 μm^2 for the PLA/PHBV nodules), confirming the compatibilizing effect of oLA.

Table 4. PHVB and PHBV/oLA nodules size in PLA film

Nodules	Mean area [μm^2]	Mean width [μm]	Mean length [μm]
PLA/PHBV	0.14±0.09	0.27±0.09	0.59±0.06
PLA/PHBV/oLA 1 wt%	0.11±0.10	0.26±0.12	0.50±0.26

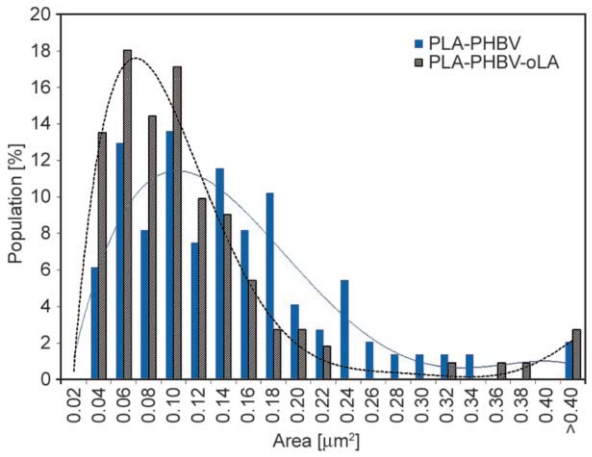

Figure 5. PHBV nodule size repartition in PLA/PHBV and PLA/PHBV/oLA 1 wt% blends. Shapes of the distributions are eyeguides only

3.3.3. Mechanical properties

The results of mechanical analysis for PLA/PHBV and PLA/PHBV/oLA with different amount of oLA films are summarized in Table 5 and representative stress strain curves are reported in Figure 6.

The addition of small amounts of oLA reveal a slight improvement in the Young's modulus (E_{Young}) over PLA/PHBV (around 10%) while no effect is observed for single PLA, which may be linked to the increase in the crystallinity of the PHBV nodules. Yield strength however, remains similar for all the samples tested. The elongation at break (ε_b) of PLA/PHBV films strongly increases with the addition of PLA short chains (Table 3), showing an important enhancement in blends ductility. Films with 1 wt% oLA shows the highest elongation at break.

Table 5. Results from tensile test for PLA, PLA/oLA and PLA/PHBV films as a function of the amount of oLA [wt%]

Samples	Mechanical properties		
	σ_y [MPa]	ε_b [%]	E_{Young} [MPa]
PLA	45±4	3.1±1.0	2050±481
PLA/oLA 1%	48±7	2.8±0.5	2107±210
PHBV*	39	2.0	3500–2800
PLA/PHBV	43±5	3.0±1.0	2507±252
PLA/PHBV/oLA 0.1%	47±1	8.0±2.0	2747±452
PLA/PHBV/oLA 0.5%	45±4	6.0±1.0	2709±382
PLA/PHBV/oLA 1%	44±2	14.0±3.0	2799±133

*http://www.tianan-enmat.com/pdf/TDS_Y1000P_Dec2011.pdf. 2011

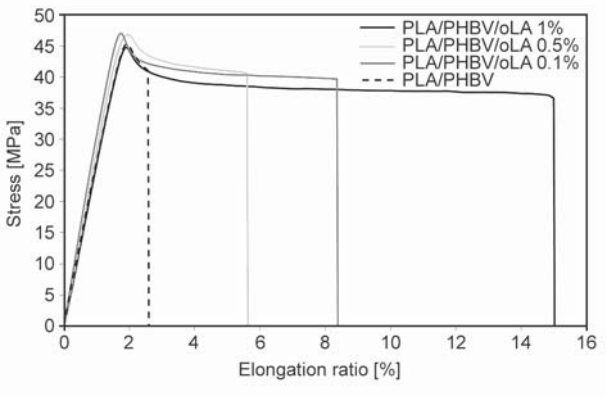

Figure 6. Traction curves for the PLA/PHBV blends as a function of the amount of oLA [wt%]

This improved elongation at break can be interpreted by two ways: The first explanation is that the oLA acts as a compatibilizer so it creates an interphase between the PLA and PHBV facilitating stress transmission at the interface. The second explanation is based on the fact that the oLA acts as a plasticizer. A non-significant evolution in elongation at break from 3.1% for the neat PLA to 2.8% for PLA/oLA (99/1) blend is observed. This result shows that the plasticizing effect is negligible for the PLA phase and the compatibilizing effect of the oLA led to the improvement of the elongation at break for PLA/PHBV/oLA films.

Tan δ evolutions obtained by DMTA are shown in Figure 7 for neat PLA, PLA/PHBV and PLA/PHBV/oLA films. Neat PLA has a T_g equal to 61 °C (in agreement with DSC measurements) and, as expected, all the PLA/PHBV/oLA films display a lower glass transition temperature compared to neat PLA. As already observed in DSC results, the presence of oLA chains in the PLA/PHBV blend does have a slight effect on the glass transition temperature of PLA which can be attributed to an increased compatibility

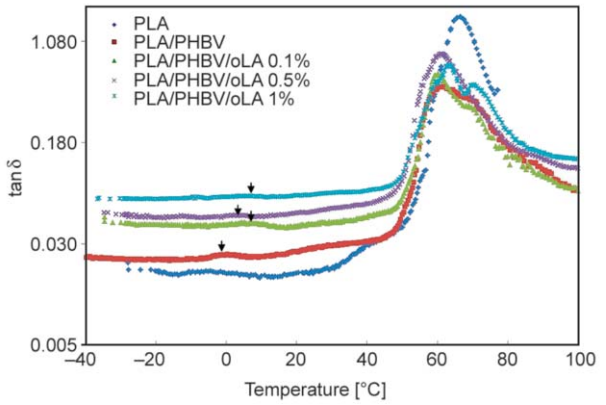

Figure 7. Temperature dependence of tan δ for neat PLA, PLA/PHBV and PLA/PHBV/oLA blends (DMA tests performed at 1 Hz). T_gs of PHBV are indicated by the black arrows.

of PLA and PHBV due to the oLA chains. Tan δ also shows a slight increase of T_g of PHBV that can be seen from –2 °C for PLA/PHBV films to a value ranged between 2 and 5 °C with oLA addition which confirms the enhancement of compatibility. This shift attributed to a compatibilizing effect of oLA is consistent with what has been observed for the mechanical properties.

3.3.4. Gas barrier properties

Results of helium permeability of the films are presented in Table 6. The helium permeability shows a small decrease (10%) for PLA/PHBV film compared to neat PLA. This can simply be attributed to better barrier properties of PHBV compared to PLA alone. According to the morphology, it is found that PHBV is dispersed in the form of small nodules in the PLA matrix related to an improvement of permeability because PLA crystallinity degrees is always low with or without oLA.

Increasing the amount of oLA in PLA/PHBV film results in a small reduction of the permeability, with a minimum (32% compared to neat PLA) obtained for the film made with 1% of oLA (see Table 6). Indeed, as the oLA amount increases, the PHBV degree of crystallinity increases which counterbalances the decrease in the size of the nodules described above, to impact beneficially the gas barrier properties even if oLA acts also as a plasticizer.

4. Conclusions

The effect of a small amount of oLA on the morphology, thermomechanical and gas barrier properties of PLA/PHBV extruded films (90–10 wt%) was studied. The miscibility of those oligomers with both polymers improved the compatibility of PLA with PHBV, which was confirmed by a drop in the interfacial tension from 0.5 to 0.3 mN/m with only 1 wt% of oLA in the PHBV dispersed phase. This also resulted in a decrease in the size of PHBV domains and a shift of both T_gs in the blends. An unexpected plastification

Table 6. Helium film permeability as a function of the amount of oLA [wt%]

	P_{He} [10^{-18} ($m^3 \cdot m$)/($m^2 \cdot s \cdot Pa$)]
PLA	136.5±5.9
PLA/PHBV	125.2±0.4
PLA/PHBV/oLA 0.1%	112.3±16.2
PLA/PHBV/oLA 0.5%	101.6±2.3
PLA/PHBV/oLA 1%	92.5±12.8

of the PHBV dispersed phase was also confirmed by an increase in the degree of crystallinity of PHBV. These combined effects resulted in films displaying much higher elongation at break (from 3 to 14% with 1 wt% of oLA) along with a slight increase in the Young's modulus. Moreover, the increase in cristallinity of PHBV also leads to a decrease of 30% of the permeability of the films.

Acknowledgements

The authors wish to thank M. Boujelben and I. Charfeddine who helped for the extrusion and the DSC measurements.

References

[1] Auras R., Harte B., Selke S.: An overview of polylactides as packaging materials. Macromolecular Bioscience, **4**, 835–864 (2004). https://doi.org/10.1002/mabi.200400043

[2] Garlotta D.: A literature review of poly(lactic acid). Journal of Polymers and the Environment, **9**, 63–84 (2001). https://doi.org/10.1023/A:1020200822435

[3] Madhavan Nampoothiri K., Nair N. R., John R. P.: An overview of the recent developments in polylactide (PLA) research. Bioresource Technology, **101**, 8493–8501 (2010). https://doi.org/10.1016/j.biortech.2010.05.092

[4] Drumright R. E., Gruber P. R., Henton D. E.: Polylactic acid technology. Advanced Materials, **12**, 1841–1846 (2000). https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E

[5] Anderson K. S., Schreck K. M., Hillmyer M. A.: Toughening polylactide. Polymer Reviews, **48**, 85–108 (2008). https://doi.org/10.1080/15583720701834216

[6] Liu H., Zhang J.: Research progress in toughening modification of poly(lactic acid). Journal of polymer science part B: Polymer Physics, **49**, 1051–1083 (2011). https://doi.org/10.1002/polb.22283

[7] Kfoury G., Raquez J-M., Hassouna F., Odent J., Toniazzo V., Ruch D., Dubois P.: Recent advances in high performance poly(lactide): From 'green' plasticization to super-tough materials *via* (reactive) compounding. Frontiers in Chemistry, **1**, 32/1–32/46 (2013). https://doi.org/10.3389/fchem.2013.00032

[8] Rasal R. M., Janorkar A. V., Hirt D. E.: Poly(lactic acid) modifications. Progress in Polymer Science, **35**, 338–356 (2010). https://doi.org/10.1016/j.progpolymsci.2009.12.003

[9] Avella M., Martuscelli E., Raimo M.: Review properties of blends and composites based on poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers. Journal of Materials Science, **35**, 523–545 (2000). https://doi.org/10.1023/A:1004740522751

[10] Noda I., Satkowski M. M., Dowrey A. E., Marcott C.: Polymer alloys of nodax copolymers and poly(lactic acid). Macromolecular Bioscience, **4**, 269–275 (2004). https://doi.org/10.1002/mabi.200300093

[11] Ma P., Spoelstra A. B., Schmit P., Lemstra P. J.: Toughening of poly (lactic acid) by poly (β-hydroxybutyrate-*co*-β-hydroxyvalerate) with high β-hydroxyvalerate content. European Polymer Journal, **49**, 1523–1531 (2013). https://doi.org/10.1016/j.eurpolymj.2013.01.016

[12] Bartczak Z., Galeski A., Kowalczuk M., Sobota M., Malinowski R.: Tough blends of poly(lactide) and amorphous poly([R,S]-3-hydroxy butyrate) – Morphology and properties. European Polymer Journal, **49**, 3630–3641 (2013). https://doi.org/10.1016/j.eurpolymj.2013.07.033

[13] Lim J. S., Park K-I., Chung G. S., Kim J. H.: Effect of composition ratio on the thermal and physical properties of semicrystalline PLA/PHB-HHx composites. Materials Science and Engineering: C, **33**, 2131–2137 (2013). https://doi.org/10.1016/j.msec.2013.01.030

[14] Zhang M., Thomas N. L.: Blending polylactic acid with polyhydroxybutyrate: The effect on thermal, mechanical, and biodegradation properties. Advances in Polymer Technology, **30**, 67–79 (2011). https://doi.org/10.1002/adv.20235

[15] Ferreira B. M. P., Zavaglia C. A. C., Duek E. A. R.: Films of PLLA/PHBV: Thermal, morphological, and mechanical characterization. Journal of Applied Polymer Science, **86**, 2898–2906 (2002). https://doi.org/10.1002/app.11334

[16] Nanda M. R., Misra M., Mohanty A. K.: The effects of process engineering on the performance of PLA and PHBV blends. Macromolecular Materials and Engineering, **296**, 719–728 (2011). https://doi.org/10.1002/mame.201000417

[17] Boufarguine M., Guinault A., Miquelard-Garnier G., Sollogoub C.: PLA/PHBV films with improved mechanical and gas barrier properties. Macromolecular Materials and Engineering, **298**, 1065–1073 (2012). https://doi.org/10.1002/mame.201200285

[18] Zembouai I., Kaci M., Bruzaud S., Benhamida A., Corre Y-M., Grohens Y.: A study of morphological, thermal, rheological and barrier properties of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/polylactide blends prepared by melt mixing. Polymer Testing, **32**, 842–851 (2013). https://doi.org/10.1016/j.polymertesting.2013.04.004

[19] Blümm E., Owen A. J.: Miscibility, crystallization and melting of poly(3-hydroxybutyrate)/poly(L-lactide) blends. Polymer, **36**, 4077–4081 (1995). https://doi.org/10.1016/0032-3861(95)90987-D

[20] Koyama N., Doi Y.: Miscibility of binary blends of poly[(R)-3-hydroxybutyric acid] and poly[(S)-lactic acid]. Polymer, **38**, 1589–1593 (1997). https://doi.org/10.1016/S0032-3861(96)00685-4

[21] Zhang L., Xiong C., Deng X.: Miscibility, crystallization and morphology of poly(β-hydroxybutyrate)/poly (D,L-lactide) blends. Polymer, **37**, 235–241 (1996). https://doi.org/10.1016/0032-3861(96)81093-7
[22] Gerard T., Budtova T.: Morphology and molten-state rheology of polylactide and polyhydroxyalkanoate blends. European Polymer Journal, **48**, 1110–1117 (2012). https://doi.org/10.1016/j.eurpolymj.2012.03.015
[23] Gérard T., Budtova T., Podshivalov A., Bronnikov S.: Polylactide/poly(hydroxybutyrate-*co*-hydroxyvalerate) blends: Morphology and mechanical properties. Express Polymer Letters, **8**, 609–617 (2014). https://doi.org/10.3144/expresspolymlett.2014.64
[24] Zhang J., Sato H., Furukawa T., Tsuji H., Noda I., Ozaki Y.: Crystallization behaviors of poly(3-hydroxybutyrate) and poly(L-lactic acid) in their immiscible and miscible blends. The Journal of Physical Chemistry B, **110**, 24463–24471 (2006). https://doi.org/10.1021/jp065233c
[25] Yoon J-S., Lee W-S., Kim K-S., Chin I-J., Kim M-N., Kim C.: Effect of poly(ethylene glycol)-block-poly(L-lactide) on the poly[(R)-3-hydroxybutyrate]/poly(L-lactide) blends. European Polymer Journal, **36**, 435–442 (2000). https://doi.org/10.1016/S0014-3057(99)00068-3
[26] Yang J., Zhu H., Zhang C., Jiang Q., Zhao Y., Chen P., Wang D.: Transesterification induced mechanical properties enhancement of PLLA/PHBV bio-alloy. Polymer, **83**, 230–238 (2016). https://doi.org/10.1016/j.polymer.2015.12.025
[27] Wang S., Ma P., Wang R., Wang S., Zhang Y., Zhang Y.: Mechanical, thermal and degradation properties of poly (D,L-lactide)/poly(hydroxybutyrate-*co*-hydroxyvalerate)/poly(ethylene glycol) blend. Polymer Degradation and Stability, **93**, 1364–1369 (2008). https://doi.org/10.1016/j.polymdegradstab.2008.03.026
[28] Arrieta M. P., Samper M. D., López J., Jimenez A.: Combined effect of poly(hydroxybutyrate) and plasticizers on polylactic acid properties for film intended for food packaging. Journal of Polymers and the Environment, **22**, 460–470 (2014). https://doi.org/10.1007/s10924-014-0654-y
[29] Arrieta M. P., López J., Hernández A., Rayón E.: Ternary PLA–PHB–limonene blends intended for biodegradable food packaging applications. European Polymer Journal, **50**, 255–270 (2014). https://doi.org/10.1016/j.eurpolymj.2013.11.009
[30] Abdelwahab M. A., Flynn A., Chiou B-S., Imam S., Orts W., Chiellini E.: Thermal, mechanical and morphological characterization of plasticized PLA–PHB blends. Polymer Degradation and Stability, **97**, 1822–1828 (2012). https://doi.org/10.1016/j.polymdegradstab.2012.05.036
[31] Armentano I., Fortunati E., Burgos N., Dominici F., Luzi F., Fiori S., Jiménez A., Yoon K., Ahn J., Kang S., Kenny J. M.: Processing and characterization of plasticized PLA/PHB blends for biodegradable multiphase systems. Express Polymer Letters, **9**, 583–596 (2015). https://doi.org/10.3144/expresspolymlett.2015.55
[32] D'Amico D. A., Iglesias Montes M. L., Manfredi L. B., Cyras V. P.: Fully bio-based and biodegradable polylactic acid/poly(3-hydroxybutirate) blends: Use of a common plasticizer as performance improvement strategy. Polymer Testing, **49**, 22–28 (2016). https://doi.org/10.1016/j.polymertesting.2015.11.004
[33] Li Y., Wu H., Wang Y., Liu L., Han L., Wu J., Xiang F.: Synergistic effects of PEG and MWCNTs on crystallization behavior of PLLA. Journal of Polymer Science Part B: Polymer Physics, **48**, 520–528 (2010). https://doi.org/10.1002/polb.21917
[34] Corre Y-M., Bruzaud S., Audic J-L., Grohens Y.: Morphology and functional properties of commercial polyhydroxyalkanoates: A comprehensive and comparative study. Polymer Testing, **31**, 226–235 (2012). https://doi.org/10.1016/j.polymertesting.2011.11.002
[35] Javadi A., Srithep Y., Pilla S., Clemons C. C., Gong S., Turng L. S.: Microcellular poly(hydroxybutyrate-*co*-hydroxyvalerate)-hyperbranched polymer–nanoclay nanocomposites. Polymer Engineering and Science, **51**, 1815–1826 (2011). https://doi.org/10.1002/pen.21972
[36] Zhang X., Espiritu M., Bilyk A., Kurniawan L.: Morphological behaviour of poly(lactic acid) during hydrolytic degradation. Polymer Degradation and Stability, **93**, 1964–1970 (2008). https://doi.org/10.1016/j.polymdegradstab.2008.06.007
[37] Xing P., Bousmina M., Rodrigue D., Kamal M. R.: Critical experimental comparison between five techniques for the determination of interfacial tension in polymer blends: Model system of polystyrene/polyamide-6. Macromolecules, **33**, 8020–8034 (2000). https://doi.org/10.1021/ma000537x
[38] Fischer E. W., Sterzel H. J., Wegner G.: Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. Kolloid-Zeitschrift und Zeitschrift für Polymere, **251**, 980–990 (1973). https://doi.org/10.1007/BF01498927
[39] Scandola M., Focarete M. L., Adamus G., Sikorska W., Baranowska I., Świerczek S., Gnatowski M., Kowalczuk M., Jedlinski Z.: Polymer blends of natural poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and a synthetic atactic poly(3-hydroxybutyrate). Characterization and biodegradation studies. Macromolecules, **30**, 2568–2574 (1997). https://doi.org/10.1021/ma961431y

[40] Enriquez E., Mohanty A. K., Misra M.: Biobased blends of poly(propylene carbonate) and poly(hydroxybutyrate-*co*-hydroxyvalerate): Fabrication and characterization. Journal of Applied Polymer Science, **134**, 44420/1–44420/10 (2017). https://doi.org/10.1002/app.44420

[41] Carli L. N., Crespo J. S., Mauler R. S.: PHBV nanocomposites based on organomodified montmorillonite and halloysite: The effect of clay type on the morphology and thermal and mechanical properties. Composites Part A: Applied Science and Manufacturing, **42**, 1601–1608 (2011). https://doi.org/10.1016/j.compositesa.2011.07.007

[42] Gogolewski S., Jovanovic M., Perren S. M., Dillon J. G., Hughes M. K.: The effect of melt-processing on the degradation of selected polyhydroxyacids: Polylactides, polyhydroxybutyrate, and polyhydroxybutyrate-*co*-valerates. Polymer Degradation and Stability, **40**, 313–322 (1993). https://doi.org/10.1016/0141-3910(93)90137-8

[43] Arrieta M. P., Fortunati E., Dominici F., Rayón E., López J., Kenny J. M.: Multifunctional PLA–PHB/cellulose nanocrystal films: Processing, structural and thermal properties. Carbohydrate Polymers, **107**, 16–24 (2014). https://doi.org/10.1016/j.carbpol.2014.02.044

[44] Phuong V. T., Coltelli M-B., Cinelli P., Cifelli M., Verstichel S., Lazzeri A.: Compatibilization and property enhancement of poly(lactic acid)/polycarbonate blends through triacetin-mediated interchange reactions in the melt. Polymer, **55**, 4498–4513 (2014). https://doi.org/10.1016/j.polymer.2014.06.070

[45] Tri P. N., Domenek S., Guinault A., Sollogoub C.: Crystallization behavior of poly(lactide)/poly(β-hydroxybutyrate)/talc composites. Journal of Applied Polymer Science, **129**, 3355–3365 (2013). https://doi.org/10.1002/app.39056