

High Performance Compostable Biocomposites Based on Bacterial Polyesters Suitable For Injection Molding and Blow Extrusion

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This work deals with the design, preparation and characterization of composites based on Poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate] and lignocellulosic filler suitable for the production of compostable and biodegradable biocomposites that mimic the thermo-mechanical and processing characteristics commonly found in those polymeric materials specially designed for injection molding and blow extrusion.

The best formulation in terms of processability, thermo-mechanical properties and biodegradation behavior under mature compost conditions was the biocomposite that contained 42.8 % by wt. of Poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate] as the major component, 5 % by wt. of lignocellulosic filler, 10 % by wt. of tributyl citrate plasticizer, 30 % by wt. of Poly(butylene adipate-*co*-terephthalate), 10 % by wt. of Poly(vinyl acetate), 0.2 % by wt. of Joncryl ADR-4368C a chain extender, 1 % by wt. of a primary antioxidant mix, and 1 % by wt. of nucleating agents.

Key words:

biocomposites, Poly(hydroxyalkanoate) (PHAs), processing, injection molding, biodegradation, chain extenders

Introduction

Nowadays, there is an increasing interest toward the substitution of oil-based polymers with bio-based polymers. Poly(hydroxyalkanoates) (PHAs) emerge as a new class of biopolymers, that have gained more and more attention due to their thermoplastic behaviour, acceptable mechanical properties and biodegradability in compost conditions¹. Applications based on PHAs, as a matrix, are generally found in the biomedical area due to their biocompatibility characteristic², but is now extended into short-term areas such as the production of compostable films for the collection of organic wastes, food contact applications, and injected parts.

Poly[(*R*)-3-hydroxybutyrate] (PHB) and Poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate] (PHBV) are aliphatic and biodegradable polyesters that belong to the PHAs family. The biopolymers are produced from renewable resources by using bacteria that synthesize PHAs as an energy feedstock. PHB, as well as PHBV, are thermoplastic polymers characterized by a high crystallinity content, hydrophobic behaviour, and are completely biodegradable in soil and compost conditions^{1,3,4}.

Moreover, both PHB and PHBV have a high melting temperature and a high resistance to organic solvents¹.

The main drawbacks of the use of PHAs for applications where a good balance between the mechanical properties and processability is required, are:

- PHAs have a low melt strength due, in part, to the lack of physical and chemical crosslinking points.

- The degradation window for PHB and its copolymers is narrow and in several cases, the melting temperature of PHB is close to its thermal degradation temperature⁵.

- Narrow distribution of its molecular weight due to its particular synthetic route (bacterial)⁶.

- In solid state, PHB is characterized by a large crystalline structure (spherulites) that makes it rigid and brittle due to its low nucleation density¹.

- Aging behavior has been observed during storage at room temperature⁷.

Moreover, dramatic structural changes have been observed, in terms of reduction of the initial molecular weight of the polymer, by the presence of water molecules that promote chain breakdown reactions⁸ and by catalytic reactions involving the

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PHB end groups and crotonic acid molecules⁹. For some applications, the progressive loss of the molecular weight during processing can be considered as a problem that must be faced and resolved.

Therefore, in order to improve the mechanical properties of PHB and PHBV biocomposites as well as their processing characteristics, three different strategies have been adopted in this study: 1) Plasticization with compatible and biodegradable plasticizer together with nucleating agents; 2) Blending with miscible and biodegradable polymers; 3) Combination of strategy 1 and 2. In particular, a reactive additive (Joncryl ADR-4368C¹⁰) has been used, that is able to control the molecular weight loss of the biopolymer during processing while it reacts with the functional groups presents in the molten state, thus increasing the melt strength of the final biocomposite. For further improvement of the mechanical properties of PHBV biocomposites, a PHBV grade with a higher amount of hydroxyvalerate (3HV) units¹¹ was used.

From the literature, different strategies have been adopted to process the PHB homopolymer as well as its copolymers for several applications, such as injection moulded parts, thermoformed parts, and thin films by melt blow extrusion. In particular, the most widely suggested strategy has been the plasticization of PHB with compatible plasticizers together with the use of nucleating agents^{12,13,14}. Also, the preparation of blends of PHB with miscible polymer is another common strategy to produce new materials with outstanding properties^{12,15,16,17}.

The present research article deals with the design, preparation and characterization of PHBV biocomposites suitable for the production of injected parts and thin films while maintaining the biodegradable characteristics of the matrix, and for the first time, by using reactive blending as a strategy to improve the melt strength of the starting biopolymer. In order to produce composites with outstanding characteristics, the first approach was based on a deep characterization of the starting PHBV biopolymers followed by a cross-analysis between the processing characteristics of the biocomposites prepared and their ultimate thermo-mechanical features.

Experimental part

Materials

The starting biopolymers are commercial PHBV, named ENMAT Y1000 (PHBV), TianAn Biopolymer (China) and Ecomann PHA10021, EM (China), respectively. ENMAT Y1000 in the form of a white powder is characterized by a content of hydroxyvalerate units ranging from 2.3 – 2.5 % in mol as determined by ¹H-NMR, and by an elevated

molecular weight (450 kDa). The Ecomann PHA EM10021 (PHBV_13 % HV) in the form of pellets is characterized by a content of hydroxyvalerate units ranging from 10 – 15 % in mol as determined by ¹H-NMR. Poly(butylene adipate-co-terephthalate) (PBAT), ECOFLEX C1200, was kindly supplied by BASF – Germany. Poly(vinyl acetate) (PVAc) was purchased from Sigma-Aldrich and is characterized by a molecular weight of 140 kDa.

Hazelnut shells powder, characterized by a lignin (LN) content around 40 % by weight and by a particle size lower than 40 un (micron), was kindly supplied by Ferrero S.p.A. Italy. Plasticizers tributyl citrate (TBC) and triethyl citrate (TEC) were purchased from Sigma-Aldrich and A.C.E.F Italy, respectively. The melt strength enhancer, Joncryl ADR-4368C (J or Joncryl), was kindly supplied by BASF- Germany. A mix of antioxidants consisting of 50 % by wt. of pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (ANOX 20) and 50 % by wt. of tris(2,4-di-tert-butylphenyl) phosphite (ALKANOX 240) was kindly supplied by Ecopol S.p.A – Italy. Calcium carbonate was used as an inorganic nucleating agent and purchased from OMYA – Italy, while saccharine, an organic nucleating agent, was purchased from Sigma-Aldrich.

Composite preparation

All components were dry-blended by using a dry blend unit at 2 rpm for 35 minutes at room temperature. The blends were then dried in an oven at 80 °C over night (in order to remove the moisture) just prior to use in the Brabender Plastograph internal melt mixer. Table 1 lists the compositions of the composites designed, whereas in Table 2 their reference blends are collected. In particular, the composites contained the polymeric chain extender Joncryl ADR-4368C, here named Joncryl or J, and dispersed at room temperature in a mixer for 35 minutes immediately after their oven-drying and before their melt blending.

The composites were melt-blended by using an internal mixer chamber (volume 55 ml) connected to a plastograph Brabender recorder. The processing conditions for all PHBV-based composites were 30 rpm and 7 to 10 min at 170 °C. The Joncryl was added in all blends as melt enhancer, compatibilizer agent and as a polymeric chain extender. The torque trend and the temperature vs. time of the experiment was recorded by on-line computer.

The amount of the following additives was the same for all the biocomposites prepared: mix of antioxidants (ANOX 20 + ALKANOX 240) 1 % – wt., calcium carbonate (CaCO₃) 0.8 % – wt., saccharine 0.2 % – wt., and the amount of Joncryl was 0.2 % – wt.

Table 1 – Compositions of the investigated composites

Biocomposite	Composite components					
	PHBV (%-wt)	PVAc (%-wt)	PBAT (%-wt)	Lignin (%-wt)	TBC (%-wt)	TEC (%-wt)
F1	35.8	10	24	20.0	8.0	–
F2	42.8	10	30	5.0	10.0	–
F3	52.0	–	35	–	10.8	–
F4	48.0	–	32	17.8	–	–
F5	80.0	–	–	–	17.8	–
F6	57.8	–	40	–	–	–
F2_TEC	42.8	10	30	5.0	–	10
F2_PHBV_13 % HV*	42.8	10	30	5.0	–	10
F2_Base*	76.0*	16	–	–	5.5	–

*The matrix was the biopolymer with higher amount of HV units: PHBV(13 % HV)

Table 2 – Compositions of the reference blends

Reference name	PHBV* (%-wt)	PVAc (%-wt)	PBAT (%-wt)	Lignin (%-wt)	TBC (%-wt)	Joncryl (%-wt)
PHBV + PVAc 20 %	80	20	–	–	–	–
PHBV + PBAT 40 %	60	–	40	–	–	–
PHBV + LN 5 %	95	–	–	5	–	–
PHBV + LN 10 %	90	–	–	10	–	–
PHBV + LN 20 %	80	–	–	20	–	–
PHBV + TBC 10 %	90	–	–	–	10	–
PHBV + TBC 20 %	80	–	–	–	20	–
PHBV + TBC 30 %	70	–	–	–	30	–
PHBV + J 0.2 %	99.8	–	–	–	–	0.2
PHBV + J 5 %	95	–	–	–	–	5

*Biopolymer with lower amount of HV units (2.3 – 2.5 % mol)

Characterization techniques

Thermo-gravimetric analyses (TGA-DTG) were performed with a Mettler Thermogravimetric Analyzer TA500 equipped with a Mettler TG50 furnace and a Mettler M3 microbalance. About 10 mg of the sample was heated from 30 °C to 700 °C at a heating rate of 10 °C min⁻¹, in an air atmosphere (flux about 80 mL min⁻¹) and nitrogen atmosphere (about 60 mL min⁻¹). The onset temperature (T_{onset}), at which the material starts to decompose, was determined as the temperature corresponding to the tangent's intersection on both sides of the decomposition trace (corresponding to 10 % of weight loss). The residue was determined as the residual weight at the end of the experiment.

The differential calorimetric analyses (DSC) were done on samples (5–10 mg) by using a Differential Scanning Calorimeter Mettler-Toledo, DSC Model-822 equipped with a sensor FRS5 connected

to a STAR^e software. The sample was placed in 40 µL aluminum pans, while an empty one was used as reference. The temperature calibration was performed by utilizing indium, iron and zinc as standards. The measures were done under nitrogen flow and 10 °C min⁻¹.

The mechanical properties, in tensile mode, of the single biopolyester, the reference blends and the biocomposites were determined by using a universal tensile machine Instron 5564 with the specimen in the form of a dog-bone (dimensions: 19 mm length, 5 mm width and 0.4 – 0.5 mm of thickness) with a deformation rate equal to 2 mm min⁻¹ (according to ASTM D882 – 10¹⁸). All samples were tested at room temperature, a minimum of five samples were analysed, and average values of the mechanical properties were recorded. The samples were conditioned under controlled humidity with Mg(NO₃)₂ · 6H₂O for 3 days before being tested.

The film for the mechanical test was done by compression molding using a press P200E Collin during 10 minutes at 180 °C under a variable pressure program for the reference samples. The processing temperature for the biocomposites was 160 °C. Extensive degradation was avoided by reducing processing temperature from 180 °C to 160 °C in the case of formulated PHBV and by applying half the time necessary to complete the cycle at high pressure and temperature for all the samples. In fact, the first 5 minutes of the molding cycle was only for softening the sample.

Experimental setup for biodegradation experiments

Soil burial tests

A soil burial respirometric test, specifically set up according to ISO 17556¹⁹ and ASTM D5988²⁰ standard tests, was employed to investigate the ultimate biodegradation behavior of PHBV biocomposites and some of the relevant reference blends. In this test, the soil was mixed with a hygroscopic inert mineral substrate (Perlite – purchased from Perlite Italiana srl – Italy) that ensured satisfactory incubation conditions and a more favorable signal-to-noise ratio, resulting in improved accuracy. In particular, when limited carbon dioxide emissions are expected from the mineralization processes of the samples²¹.

A natural forest soil sample, sieved until reaching a particle size smaller than 1 mm (ASTM sieve Mesh n° 18), was used as incubation substrate because its richness in microbial population is able to metabolize a wide spectrum of organic compounds. The sieved soil was mixed with hygroscopic inert Perlite mineral in a weight ratio of 2:1. An amount of distilled water equivalent to the weight of Perlite was then dropped into the previous mix in order to adjust the water holding capacity (WHC) according to ASTM D5988²⁰. The amount of distilled water was corrected by considering the amount of water present in the soil –Table 3. The moisturized blend

Table 3 – Physical and chemical characteristics of the soil used in the biodegradation test

Parameter	Value	
Type	Unit	
Electrical conductivity*	dS m ⁻¹	0.15
pH	–	6.71
Total nitrogen	%	0.159
Total organic carbon	%	1.465
Total inorganic carbon	%	0.011
Water holding capacity (WHC)	%	20.0
Humidity	%	8.35

*Electrical conductivity (distilled water: soil, 5:1 by weight)

of soil/Perlite was mixed manually until a homogeneous mixture was reached.

The tests were carried out in cylindrical glass vessels (Biometer flask – 750 mL capacity) containing a multilayer substrate in which the pre-treated soil was mixed with PHBV-based samples in powder (particle size < 2 mm – mesh n° 10 ASTM sieve). The PHBV-based samples and the reference sample (cellulose) were tested at approximately 50 mg g⁻¹ dry soil ratio, in duplicate runs. The blend was then placed between two layers of hydrated Perlite; the test vessels were incubated at room temperature and kept in the dark.

Cellulose powder was used as a reference compound with the aim to validate the adopted test procedure.

The soil burial biodegradation test was performed for PHBV biocomposites consisting of lignin from hazelnut shells as organic filler, the polymeric chain extender Joncryl, and a combination of both components. Joncryl was investigated because it is a special additive, and it is important to understand the role of this additive in the biodegradation behavior of the above-mentioned samples in order to tune its amount in the final high performance biocomposite formulates. Table 4 shows the biocomposite compositions and the samples amounts used for the test.

Table 4 – Sample composition for the biodegradation test in soil burial conditions

Sample I.D. ^a	Description (% – wt.)	Replicate 1 (g)	Replicate 2 (g)	C _{org} (%- wt.)
PHBV	HV 2.3 – 2.5 mol %	0.3824	0.3801	57.7
PHBV-J5	PHBV + 5 % Joncryl	0.3803	0.3824	59.1
PHBV-LN10	PHBV + 10 % Lignin	0.3817	0.3800	55.8
PHBV-LN20	PHBV + 20 % Lignin	0.3815	0.3804	55.1
PHBV-LN10-J5	PHBV + 10 % Lignin + 5 % Joncryl	0.3813	0.3827	53.9
PHBV-LN20-J5	PHBV + 20 % Lignin + 5 % Joncryl	0.3808	0.3800	56.8
Cellulose	Cellulose powder	0.3822	0.3816	44.4
Blank	Soil medium	–	–	–

^aAnalyzed in the form of powder for all cases

Mature compost test

The respirometric tests in mature compost were done inside a glass vessel of 750 mL under controlled aerobic conditions in order to promote a direct contact between the PHBV biocomposite film and the mature compost. Each vessel was equipped with a glass beaker containing a known amount of a 0.5 mol L⁻¹ KOH solution for the absorption of the CO₂ produced during the incubation timeframe.

The mature compost was kindly supplied by Genesi S.p.A – Pontedera (Pisa – Italy) and its main chemical and physical characteristics are shown in Table 5.

The compost was pre-treated by taking 230 g of sieved compost (fresh weight) and blending it with 190 g of Perlite. It was then added 340 g of distilled water in order to fit the humidity level according to ISO 14855²⁴. All the components were then mixed manually until a homogeneous blend was reached.

A layer of hydrated Perlite (15 g of Perlite : 15 g distilled water) was placed at the bottom of the vessel, then 30 g of pre-treated compost was placed on the Perlite. Finally, the samples in the form of thin films (having a maximum area of 4 cm²) were placed on the pre-treated compost layer, the same assembly was applied to the positive control (cellulose film). The ratio between the sample and dry compost was

1:7 by weight. The vessels with the PHBV-based samples and the blank control were incubated at 58±2 °C under dark conditions for 6 months. The biodegradation extent was followed by measuring the production of CO₂ by titration of the KOH solution at periodic intervals. The tests were made in duplicate. Table 6 shows the samples selected for the study and the amount used for mature compost test.

Results and discussion

The results reported in this paper were articulated in two lines of intervention that allowed to design the biocomposite compositions and establish the strategies aimed at improving the thermo-mechanical and processing characteristics of the pristine biopolyesters, as well as to tune the final composition of the high performance biocomposite.

The first line of intervention was focused on studying the influence of the single additive on the thermo-mechanical and processing characteristics of PHBV with a low amount of HV (2.3 – 2.5 % mol). The additives under analysis were: the chain extender Joncryl, the lignocellulosic filler obtained from hazelnut shells powder (LN), and the plasticizer Tributyl Citrate (TBC). For comparison purposes, the blends with Poly(vinyl acetate) (PVAc) and Poly(butylene adipate-*co*-terephthalate) (PBAT)

Table 5 – Chemical and physical analysis of the mature compost used in the biodegradation test

Parameter	Units	Value	Limit ^{a)}	Method
Humidity at 105 °C	%	29.5	< 50 %	UNI 10780/98 ²²
pH	Log a _{H+}	7.3	6–8.5	EPA 9045D/2002 ²³
Ratio C/N	wt.	27.5	< 50	UNI 10780/98
Organic carbon	% ^{a)}	35.5	> 20	UNI 10780/98
Organic acid	% ^{a)}	7.3	> 2.5	UNI 10780/98
Organic nitrogen	% ^{a)}	87.4	> 80 % total N	UNI 10780/98
Total nitrogen	% ^{a)}	1.29	–	UNI 10780/98
Particle size	mm	> 2	70 %	–
		1 and 2	17 %	
		< 1	13 %	

^{a)}On compost dry weight

Table 6 – Selected sample weight for mature compost test

Sample I.D	Description (%-wt)	Replicate 1 (mg)	Replicate 2 (mg)	C _{org} (% – wt.)
PHBV	HV 2.3 – 2.5 mol %	146.4	134.1	57.5
PHBV-J5	PHBV + 5 % Joncryl	145.0	149.2	59.1
PHBV-J0.2	PHBV + 0.2 % Joncryl	148.9	167.3	57.7
PHBV-LN20	PHBV + 20 % Lignin	148.3	142.5	55.1
PHBV-LN20-J5	PHBV + 20 % Lignin + 5 % Joncryl	146.1	148.3	53.9
F2	See Table 1	152.1	151.3	55.6
F5	See Table 1	142.1	152.7	55.5
Cellulose	Film	144.7	153.7	43.9

at fixed composition were additionally prepared. Particular attention was paid to the chain extender additive and its influence on the biodegradation behavior of PHBV under soil burial and mature compost conditions. The Joncryl ADR-4368C is a reactive multifunctional additive that, in accordance with its technical data sheet¹⁰, is able to control and refrain the loss of the molecular weight during processing, by reacting with the functional groups available in the molten state, thus increasing the melt strength of the final composite. This characteristic is important for the production of composites to be eventually processed by melt blow extrusion. Other crucial additives were also included in the biocomposite formulations: primary antioxidants (1 % – wt.) and nucleating agents (0.2 at 1 % – wt.).

The second line of intervention was based on the results obtained from the first line, in terms of the best PHBV/additive ratio. Thereby, three strate-

gies were adopted aimed at building up, in a unique solution, a biocomposite suitable for injection molding and blow extrusion with outstanding thermo-mechanical characteristics by maintaining the biodegradation behavior of the major component (PHBV). Thus, the strategies selected were: 1) Plasticization of PHBV with compatible and biodegradable plasticizer together with nucleating agents, 2) Blending with miscible poly(vinyl acetate) (PVAc) and biodegradable polymers poly(butylene adipate-*co*-terephthalate) (PBAT) and 3) Combination of 1 and 2.

The results obtained from the first line of intervention were divided into: a) processing characteristics, and b) thermo-mechanical properties.

Processing description

From the Torque curve evolution within the time (Fig. 1a), no significant variation was observed

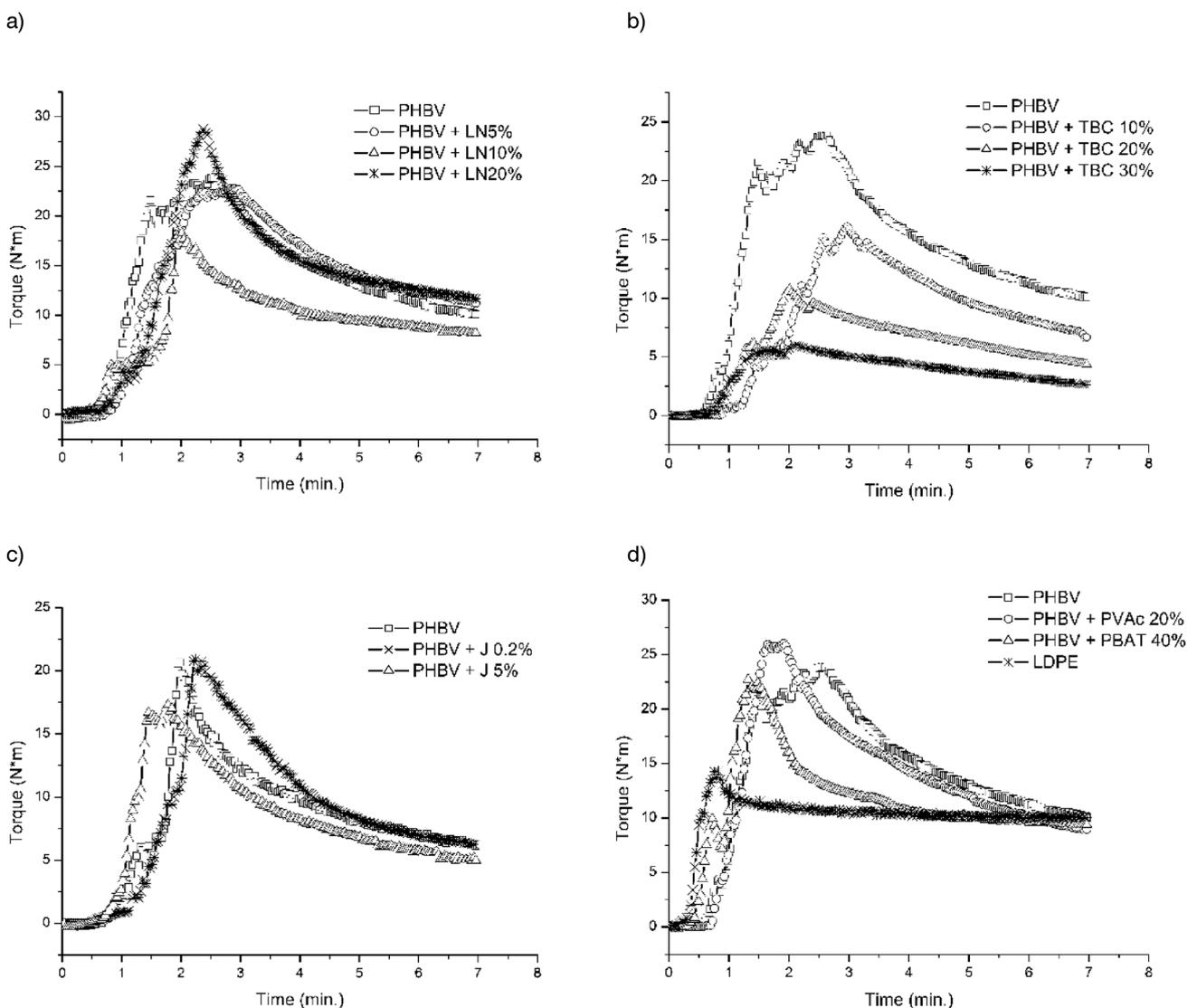


Fig. 1 – Torque evolution within time for PHBV blends with: a) Lignin from hazelnut shells (LN), b) Plasticizer TBC, c) Chain extender Joncryl, and d) PVAc, PBAT

on the Torque behavior by varying the amount of organic filler LN (5 %, 10 % and 20 % – wt.). However, by adding 10 % by wt. of LN a slight Torque stabilization was observed at higher residence time. Then, the best weight ratio of PHBV/LN selected was 9.

The lignocellulosic organic filler, in the form of powder, was obtained directly from ground hazelnut shells that, according to Demirbaş²⁵, has 42.8 % – wt. of lignin (major component), 30.4 % – wt. of hemicellulose and 26.8 % – wt. of cellulose. Brown, rigid and brittle biocomposites were obtained with the use of LN as organic filler.

The addition of plasticizer TBC (10 %, 20 % and 30 % by wt.) into the PHBV produces a clear reduction of the Torque during the entire processing range (Fig. 1b). The higher the amount of TBC, the higher was the reduction of the Torque evolution. However, a content of 20 % – wt. was selected as the best amount of plasticizer. A slight stabilization of the Torque at higher residence time was observed, thus giving a weight ratio PHBV/plasticizer equal to 4. At 30 % – wt. of TBC a migration of plasticizer was observed, thus suggesting poor compatibility between the selected plasticizer and the PHBV.

A reduction of the Torque with time was also obtained by adding the chain extender additive at a different concentration: 0.2 % and 5 % – wt. Nevertheless, the amount of 0.2 % – wt. of Joncryl produces a Torque curve resembling the PHBV torque

curve, suggesting a better dispersion of the additive in the molten phase. Then, the amount of the Joncryl selected was 0.2 % – wt. (Fig. 1c).

A remarkable improvement in the Torque behavior with time was observed by using 40 % – wt. of PBAT. The Torque behavior resembles the torque curve of a Low Density Poly(ethylene) LDPE grade Riblene® FL23. That LDPE sample is loaded with slip agent, suitable for blown film extrusion, and is also characterized by a good balance between processability and mechanical properties. The Torque curve for the sample containing 20 % – wt. of PVAc resembles the Torque curve of the raw PHBV sample. Then, the pre-selected ratios for PHBV/PBAT was 1.5, and 4 for PHBV/PVAc.

Thermo-mechanical properties

Table 7 shows the results of thermo-gravimetric analysis (TGA-DTG) for the single components, the reference blends, and the PHBV biocomposites. A slight reduction of around 5–6 degrees in the temperature at which a maximum rate of degradation (DTG- T_{p1}) occurs, was observed for the samples containing LN at variable amounts. This suggests that the LN organic filler promotes an early degradation of PHBV. Nonetheless, the PHBV composite with 10 % of LN shows a higher onset of the degradation temperature, indicating a better thermal stability. The TGA-DTG analysis was conducted only for the sample with 20 % – wt. of TBC. A reduction was observed in the onset temperature as well as in

Table 7 – TGA analysis and derivative weight loss (DTG) results conducted in air for the single components, PHBV reference blends, and biocomposites

Sample I.D ^{a)}	TGA		DTG			
	$T_{10\%}$ (°C)	Residue (%)	T_{p1} (°C)	T_{p2} (°C)	T_{p3} (°C)	T_{p4} (°C)
PHBV	259	0.42	283	–	–	–
PHBV_13 % HV	266	11.8	203	285	334	431
Joncryl (J)	241	0.18	328	345	416	499
Lignin (LN)	260	1.15	323	435	–	–
PBAT	363	0.21	399	500	–	–
PHBV + J0.2 %	256	0.40	280	–	–	–
PHBV + J5 %	251	0.46	276	–	–	–
PHBV + PVAc20 %	260	0.40	280	329	473	–
PHBV + PBAT40 %	252	0.16	269	396	483	–
PHBV + LN5 %	260	0.33	278	–	–	–
PHBV + LN10 %	261	0.46	276	–	–	–
PHBV + LN20 %	260	0.44	277	–	–	–
PHBV + TBC20 %	238	0.23	236	287	–	–

^{a)}A content of 2.3–2.5 % mol of HV units in the PHBV unless stated otherwise

the maximum temperature (T_{p1}) at which a maximum rate of degradation also occurs, thus indicating an early degradation of the plasticizer sample compared to the pure PHBV. The thermal stability of PHBV was also slightly reduced by the presence of the chain extender additive Joncryl. Nevertheless, at 0.2 % – wt. the reduction was lower than the sample containing 5 % – wt. of Joncryl, thus suggesting that, at lower load levels of Joncryl, a better thermal stability was obtained for the biopolyester. Finally, the thermal stability of PHBV blended with PVAc was similar to that of the pure PHBV, while the blend with PBAT was less thermally stable.

Table 8 shows the results obtained through differential scanning calorimetric analysis (DSC) for the single components, the reference blends, and the PHBV biocomposites. By increasing the amount of LN, the degree of crystallinity in the PHBV was reduced, the sample with 20 % – wt. of LN, instead, showed a higher crystallinity compared to the pure biopolymer. The melting temperature peak (T_m) increases in the PHBV with the addition of LN. This fact can represent an adverse characteristic, considering that the melting temperature of the pure polymer is closer to its degradation temperature. Thus, even if the increase is 4–5 °C, this will be enough to promote the degradation of the sample.

The TBC plasticizer was unable to modify the glass transition temperature (Table 8) of the PHBV upon heating, and the final plasticized sample remained rigid and fragile even when an elevated amount of plasticizer was added. Moreover, a similar behavior on the thermogram curves was obtained at different load of TBC (results not shown). Only a reduction in the crystallinity was detected by adding the plasticizer, being 30 % – wt. the amount that produces the higher crystallinity change.

At 5 % – wt. of chain extender additive, the presence of a T_g value in the PHBV was observed, as well as a cold crystallization and a considerable reduction in crystallinity. On the contrary, at 0.2 % – wt. of Joncryl, an increment of T_m and a reduction in crystallinity were found. Both PBAT and the PVAc were able to modify the thermal behavior of the biopolyester upon heating. In the case of PVAc, a T_g and a cold crystallization temperature were observed suggesting good compatibility between the PHBV and PVAc. Additionally, a reduction in the final crystallinity was obtained for the blend with PVAc (10 % less) and PBAT (15 % less).

Regarding the mechanical properties (Table 9), not all the reference blends were susceptible to analysis, because they were fragile under the adopted tensile conditions. Moreover, the pure biopolyes-

Table 8 – Thermal properties measured during the cooling steps and second heating DSC scans of single components, PHBV, and reference blends

Sample I.D ^{a)}	T_g (°C)	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	X_c^b (%)
PHBV	n.d ^{c)}	84	103	165	117	80
PBAT	-31	39	27	120	21	-
PVAc	43	-	-	-	-	-
PHBV + LN5	n.d	93	83	168	100	72
PHBV + LN10	n.d	93	81	168	97	74
PHBV + LN20	n.d	94	81	169	95	81
PHBV + TBC10	n.d	76	79	163	97	74
PHBV + TBC20	n.d	66	60	161	98	84
PHBV + TBC30	n.d	61	50	158	75	73
PHBV + J0.2	n.d	96	92	170	107	73
PHBV + J5 ^{c)}	2	79	63	163	97	66
PHBV + PBAT40	-33	76	55	170	57	65
PHBV + PVAc20 ^{d)}	5	68	50	165	82	70

^{a)}A content of 2.3–2.5 % mol of HV units in the PHBV unless stated otherwise

^{b)} $X_c = [(\Delta H_m - \Delta H_{cc})/\Delta H_{m100} \% \cdot \theta]100$ for samples with cold crystallization, $X_c = (\Delta H_m/\Delta H_{m100} \% \cdot \theta)100$ where $\Delta H_{m100} \% \text{ crystalline} = 146 \text{ J g}^{-1}$ and θ is the weight fraction of PHBV in the formulation

^{c)} $T_{cc} = 47 \text{ °C}$, $\Delta H_{cc} = 6 \text{ J g}^{-1}$

^{d)} $T_{cc} = 54 \text{ °C}$, $\Delta H_{cc} = 10 \text{ J g}^{-1}$

^{e)}n.d = not detectable

Table 9 – Mechanical properties in tensile mode for PHBV and reference blends

Sample I.D ^{a)}	Elastic Modulus (MPa)	Young's Modulus (Tan-0.2 %) (MPa)	Tensile Strength at Yield (MPa)	Stress at Break (MPa)	Strain at Break (%)
PHB ENMAT Y1000P ²⁶	2800–3500	–	39	–	2
PHA EM10021 ^{27*}	–	–	16	–	400
PHA EM10021	546 ± 51	517 ± 65	9.9 ± 1.4	9.1 ± 1.1	8 ± 1
LDPE RIBLENE FL23	244 ± 21	227 ± 17	11.3 ± 1.2	10.1 ± 1.1	567 ± 61
LDPE SABIC	203 ± 9	188 ± 4	7.7 ± 0.6	6.9 ± 0.5	294 ± 108
PHBV + LN 5 %	2030 ± 114	2150 ± 138	35.1 ± 4.0	34.4 ± 3.2	5.1 ± 0.2
PHBV + LN 10 %	2177 ± 138	2183 ± 124	31.1 ± 3.0	29.4 ± 3.2	3.4 ± 0.2
PHBV + LN 20 %	2238 ± 112	2295 ± 63	27.5 ± 3.8	24.9 ± 2.8	1.9 ± 0.2
PHBV + PBAT40 %	847 ± 94	848 ± 91	14.1 ± 2.1	13.3 ± 1.6	5 ± 1
PHBV + TBC 30 %	762 ± 95	750 ± 100	–	11.5 ± 1.0	6 ± 2

*Values obtained from the technical data sheet, Tm DSC²⁷ 130–150 °C

^{a)}A content of 2.3–2.5 % mol of HV units in the PHBV unless stated otherwise

ter was also fragile and the values reported in Table 9 were obtained from its technical data sheet²⁶.

By adding LN into PHBV it was possible to assess the mechanical properties, in tensile mode, of the biocomposite, which was impossible to do for the PHBV due to its fragile behavior. All PHBV biocomposites studied were brittle; however, a better elongation at break (around 4 %) was obtained at 5 and 10 % of LN load. It was also possible to determine the mechanical properties for the sample having 30 % – wt. of TBC. However, at such level of TBC, as already mentioned, a clear migration of the plasticizer was observed, thus suggesting poor compatibility between the biopolyester and the selected plasticizer. All the PHBV samples containing Joncryl, in different amounts, were fragile, and it was impossible to determine their mechanical properties under tensile mode. The PBAT was able to improve the elongation at break and reduce the Young's modulus of the PHBV, suggesting a softening effect on PHBV.

Biodegradation tests in soil burial and mature compost conditions

Selected blends and composites consisting of PHBV as continuous matrix were submitted to biodegradation respirometric tests in mature compost and soil burial conditions, to ascertain the influence of the chain extender and organic filler (LN) on the biodegradation behavior.

The results obtained from mature compost tests (Fig. 2a) showed that a substantial inhibition on the biodegradation propensity did occur for the sample having 5 % – wt. of Joncryl even at long incubation time. On the contrary, in the case of the sample containing 0.2 % – wt. of Joncryl only a delay on the

biodegradation profile was observed with respect to the pure PHBV. Indeed, the sample reached the complete mineralization within 60 days according to the international norm ISO EN 13432–02²⁸.

A similar behavior was recorded during the biodegradation tests in soil burial conditions (Fig. 2b). A limited mineralization degree was observed in the case of the sample containing 5 % – wt of Joncryl with respect to pure PHBV. At 6 months incubation, the sample containing 5 % – wt of Joncryl reached only a 10 % of biodegradation compared with one fourth for PHBV and one eighth of the biodegradation detected for cellulose reference material.

The influence of the organic filler (LN) on the biodegradation behavior of PHBV was also evaluated. The sample containing 20 % – wt of LN was selected as reference sample, because at such load level, the final crystallinity of the biocomposites was similar to the pure biopolyester. It is known that the crystallinity level of PHBV samples influences the biodegradation behaviour^{11,29}. From the biodegradation profiles detected in the mature compost test (Fig. 2c), it was observed that the presence of LN (PHBV + LN20 %) does not affect negatively the biodegradation behavior under compost conditions as compared with the pure biopolyester. Interestingly, it was observed that LN filler in the sample with 5 % – wt. of Joncryl plus LN (PHBV + LN20 + J5), improved the biodegradation reaching, in two steps, 80 % of biodegradation after 110 days of incubation, whereas the sample containing only Joncryl underwent a negligible, if any, mineralization process at the same conditions and in the same time frame. An analogous trend was observed in soil burial conditions (Fig. 2d), thus finding that the

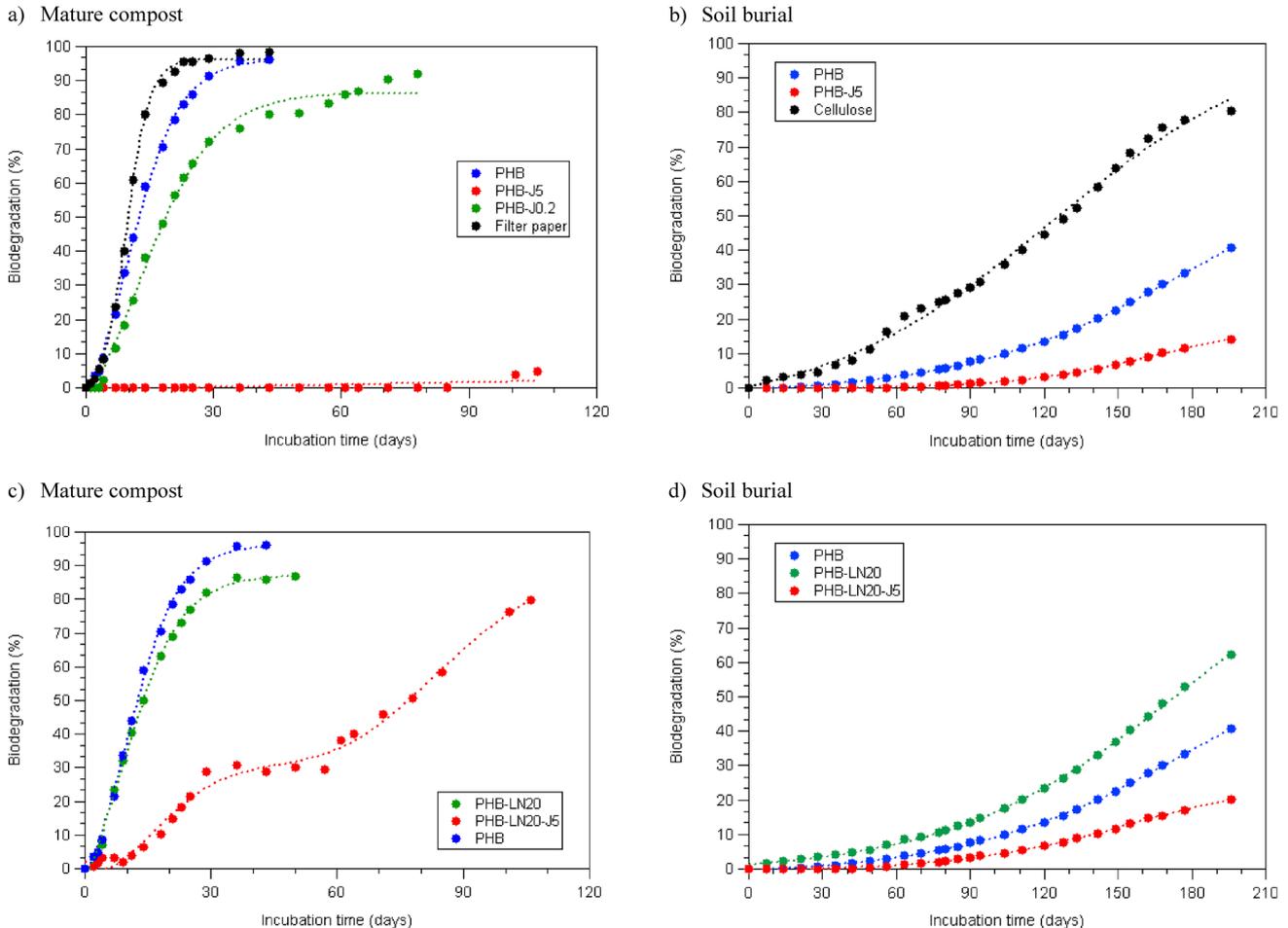


Fig. 2 – Biodegradation behavior of PHBV with chain extender (J) and lignin (LN): a) and c) in mature compost conditions, and b) and d) in soil burial conditions. PHB stands for PHBV with 2.3–2.5 % mol of HV units.

presence of LN in the sample improved the biodegradation propensity of PHBV biocomposite at higher level when compared with the pure biopolyester.

From the best results obtained from the cross-analysis of the thermal, mechanical and biodegradation behavior of the references blends and PHBV/LN biocomposites, it was possible to design 5 composite formulations and 4 PHBV plasticized blends according to the strategies established in the second line of intervention (Table 1).

The new formulations were then characterized by processing and thermo-mechanical characteristics and the biodegradation behavior of the best formulations was followed only under mature compost conditions. Fig. 3 shows the processing curve for PHBV biocomposite formulations and reference blends. Formulations 1, 2 and 3 showed the best processing behavior characterized by a stable evolution of the torque with time, with lower values of Torque resembling those of the Torque curve of LDPE grade for melt blow extrusion.

The thermal stability of the PHBV biocomposites was higher than the pure PHBV for samples F1,

Table 10 – TGA analysis conducted in air for PHBV biocomposites and PHBV plasticized blends

Sample I.D. ^{a)}	TGA Air	
	$T_{10\%}$ (°C)	Residue (%)
F1	265	1.23
F2	268	0.83
F3	257	0.90
F4	271	0.97
F5	243	0.76
F6	269	2.20
F2_TEC	276	1.02
F2_PHBV_13 % HV*	259	5.86
F2_Base*	268	8.77

*the matrix is the biopolymer with higher amount of hydroxyvalerate units: PHBV_13% HV

^{a)}Compositions reported in Table 1

F2, F4, F6, F2_TEC (Table 10, Fig. 4a). Instead, samples F3 and F5 showed a lower onset temperature probably due to the higher amount of liquid

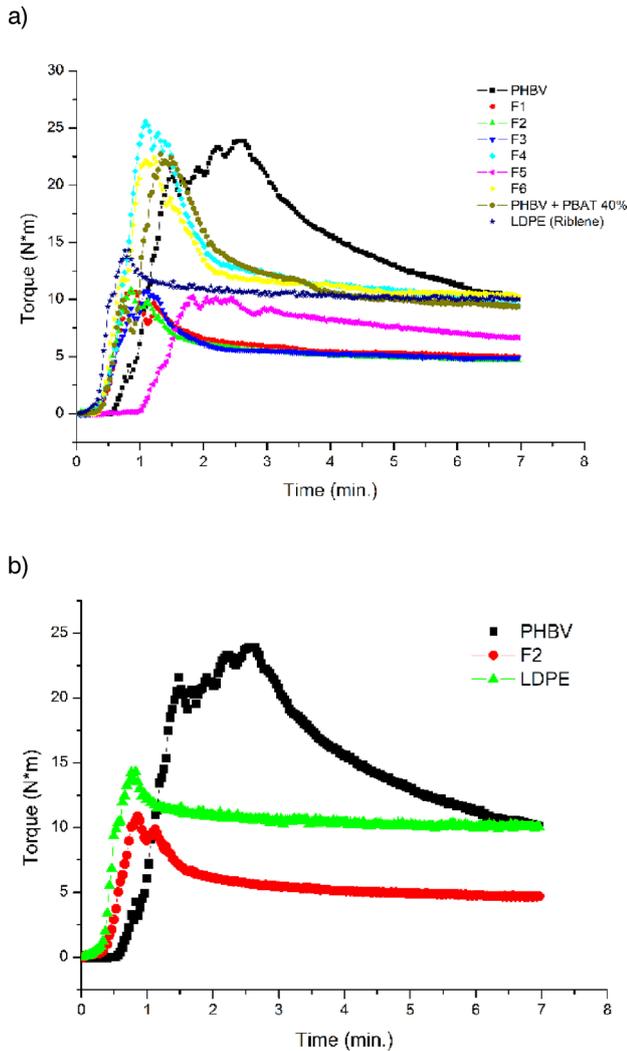


Fig. 3 – Torque evolution vs time for the biocomposite formulations: a) Reference blend, formulations and pure polymers, b) Formulation F2 and pure polymers

plasticizer (TBC) that volatilize from the biopolymer matrix during heating. The samples with the highest thermal stability were F2_TEC, in which the TBC plasticizers were substituted with triethyl citrate (TEC), followed by F4, F2 and F6. Compared with the pure PHBV, the PHBV biocomposites and PHBV plasticizer blends have multiple degradation steps (Fig. 4b) and the decomposition steps are related with the loss of plasticizer, PHBV degradation, PVAc degradation followed by the PBAT decomposition at higher temperature.

Analyzing the DSC results (Table 11), it was observed that all the PHBV biocomposites and PHBV plasticized blends are flexible at room temperature with the presence of a single T_g at values lower than 25 °C. Moreover, all of them had a cold crystallization temperature (T_{cc}) suggesting that the presence of multiple components in the formulation hindered the PHBV crystallization under controlled conditions. The sample with lower crystallinity was

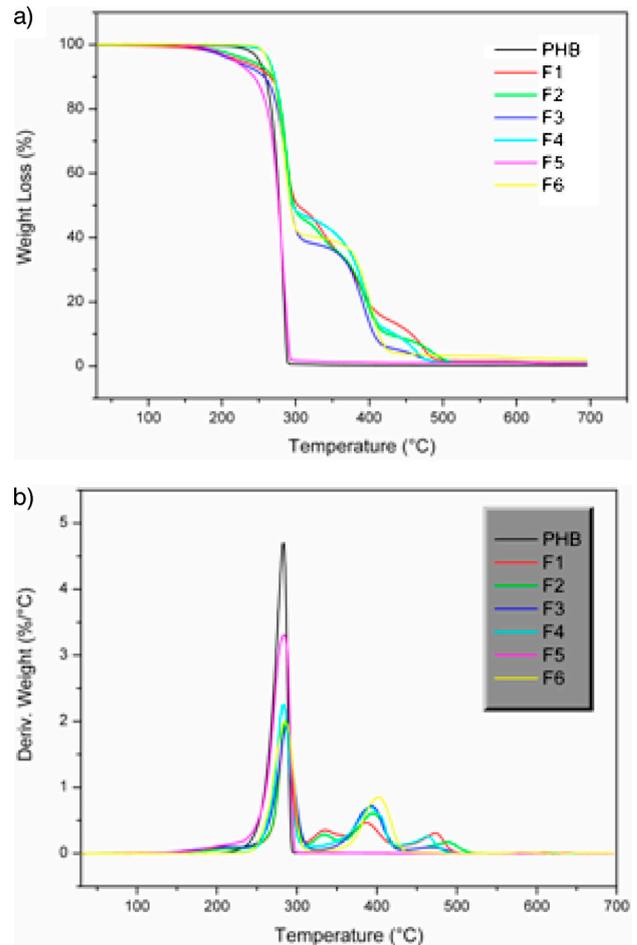


Fig. 4 – Thermogravimetric traces for PHBV biocomposites and PHBV plasticized blends: a) TGA traces, b) DTGA traces. PHB stands for PHBV with 2.3–2.5 mol of HV units.

F2, and according to the structure – properties relationship, the lower the crystallinity, the higher the propensity to deformation of the sample. Therefore, it is expected that sample F2 would show the best results in terms of mechanical properties.

In Table 12 are collected the results for the mechanical properties of the samples obtained under tensile mode. A considerable reduction was observed in the elastic modulus for all the samples compared with PHBV, even for the samples F1, F2 and F4 that contained the organic filler. The best sample in terms of elongation at break was F2. Further improvements on the F2 formulation were made by changing the type of plasticizer (sample F2_TEC), by changing the biopolyester continuous matrix (sample name F2_PHBV_13 % HV) and by eliminating the content of organic filler (sample F2_Base). By increasing the amount of HV units in the formulation, a remarkable effect on the mechanical properties was observed for the sample F2_PHBV_13 % HV with an increase in its elongation at break value by 10-fold when compared to the

Table 11 – Thermal properties from the cooling and second heating DSC scans for PHBV biocomposites and PHBV plasticized blends

Sample I.D ^{a)}	T _g (°C)	T _{cc} (°C)	ΔH _{cc} (J g ⁻¹)	T _c ^{b)} (°C)	ΔH _c (J g ⁻¹)	T _m ^{b)} (°C)	ΔH _m (J g ⁻¹)	X _c ^{c)} (%)
F1	-8	44	8	79	19	167	40	60
F2	-9	44	18	78	5	169	44	42
F3	-12	31	7	59	37	168	60	71
F4	3	47	6	83	33	173	52	66
F5	n.d ^{d)}	n.d	n.d	53	51	165	87	75
F6	4	44	15	83	30	172	65	59
F2_TEC	-7	46	13	77	17	168	42	46
F2_PHBV_13 % HV*	-21	67	16	84	4	148	7	0
F2_Base*	-17	63	23	42	4	149	17	0

^{a)}Compositions reported in Table 1

^{b)}Corresponding to the maximum peak

^{c)} $X_c = [(\Delta H_m - \Delta H_{cc}) / \Delta H_{m100} \% \cdot \theta] 100$ for samples with cold crystallization, $X_c = (\Delta H_m / \Delta H_{m100} \% \cdot \theta) 100$ where ΔH_m PHB100 % crystalline = 146 J g⁻¹ and θ is the weight fraction of PHBV in the formulation

^{d)}Not detectable

*PHBV sample used consists of 13 % mol of HV units

Table 12 – Mechanical properties in tensile mode for PHBV, reference blends, and bio-composites

Sample I.D ^{a)}	Elastic Modulus (MPa)	Young's Modulus (Tan-0.2 %) (MPa)	Tensile Stress at Yield (MPa)	Stress at Break (MPa)	Strain at Break (%)
LDPE SABIC®	203 ± 9	188 ± 4	7.7 ± 0.6	6.9 ± 0.5	294 ± 108
PHBV ²⁶	2800	–	39	–	2
PHBV_13 % HV	546 ± 51	517 ± 65	9.9 ± 1.4	9.1 ± 1.1	8 ± 1
F1	518 ± 20	518 ± 18	10.7 ± 0.8	9.8 ± 0.5	8 ± 1
F2	443 ± 11	436 ± 17	11.6 ± 0.5	10.7 ± 0.7	15 ± 2
F3	472 ± 31	471 ± 37	11.1 ± 1.3	10.0 ± 1.2	7 ± 1
F4	832 ± 25	830 ± 25	16.3 ± 1.2	14.6 ± 1.1	8 ± 1
F5	706 ± 13	704 ± 17	12.5 ± 0.3	11.2 ± 0.3	5 ± 1
F6	695 ± 31	704 ± 37	14.4 ± 1.5	12.9 ± 1.4	8 ± 1
F2_TEC	402 ± 22	403 ± 26	11.0 ± 1	9.9 ± 0.9	10 ± 2
F2_PHBV_13 % HV*	119 ± 6	107 ± 28	5.6 ± 0.2	5.0 ± 0.1	81 ± 8
F2_Base*	189 ± 7	170 ± 11	6.3 ± 0.7	5.7 ± 0.6	246 ± 59

*PHBV sample used consisting of 13 % mol of HV units unless stated otherwise

^{a)}Compositions reported in Table 1

pure biopolyester (PHBV_13 % HV). This sample can be suitable for injection molded applications; the sample F2_Base showed elastic modulus and elongation at break values similar to the LDPE that is suitable for the production of thin film by melt blow extrusion.

Finally, in order to assess the biodegradation behavior of the PHBV biocomposites with the best thermo-mechanical characteristic, the F2 was selected for test under mature compost conditions (Fig. 5). Sample F5 was also included because it has a crystalline content similar to the pristine biopolyester (PHBV). The F2 sample reached 90 % of mineralization within 90 days of incubation time, suggesting that it may fulfil compostable requirements even if its degradation behavior curve seems

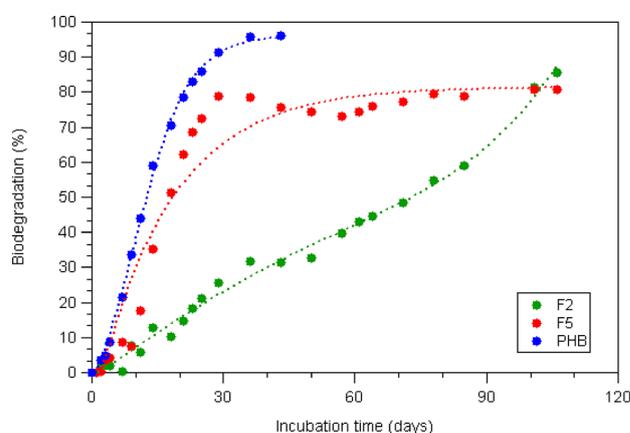


Fig. 5 – Biodegradation behavior of PHBV biocomposites F2 and F5 under mature compost conditions. PHB stands for PHBV with 2.3–2.5 % mol of HV units.

to follow the degradation in two steps. Sample F5 reached complete mineralization within 60 days, thus fulfilling compostable requirements as dictated by the norm EN-ISO 13432–02²⁸.

Conclusions

As a general conclusion, PHBV can be a promising biopolymer for the substitution of polyolefins in those applications where compostable characteristics are recommended at the end of their life cycle. However, in order to fulfil the requirements in terms of processing and thermo-mechanical properties, both in injection molding and melt blow extrusion, PHBV must be blended and formulated with compatible polymers, suitable additives, and fillers.

The best formulation in terms of processability, thermo-mechanical properties, and biodegradation behavior under mature compost conditions, was the biocomposite containing 42.8 % – wt. of PHBV, 5 % by wt. of lignocellulosic filler from hazelnut shells (LN), 10 % – wt. of TBC plasticizer, 30 % – wt. of PBAT, 10 % – wt. of PVAc, 0.2 % – wt. of chain extender (Joncryl), 1 % – wt. of primary antioxidants, and 1 % – wt. of nucleating agents. By changing the amount of HV in the PHBV and by keeping constant the composition of the above formulation, it was possible to improve the elongation at break of the final biocomposite – thus suggesting that the selected formulation is suitable for injection molding applications. It was also possible to improve the mechanical properties of PHBV by the formulation plasticized blends suitable for the production of thin films by melt blow extrusion, by combining the use of plasticizer with the compatible polymer PVAc and by increasing the amount of valerate units.

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List of abbreviations and symbols

PHAs – Poly(hydroxyalkanoates)
 PHB – Poly[(R)-3-hydroxybutyrate]
 PHBV – Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate]

3HV – 3-Hydroxyvalerate
 MW – Molecular weight
 PI – Polydispersity index
 X_c – Crystallinity fraction (%)
 ΔH_m – Enthalpy of fusion (J g⁻¹)
 $\Delta H_{m100\%}$ – Enthalpy of fusion of a 100 % crystalline reference polymer (J g⁻¹)
 rpm – Revolution per minute
 J – Joncryl ADR-4368C or Joncryl
 PVAc – Poly(vinyl acetate)
 PBAT – Poly(butylene adipate-co-terephthalate)
 LN – Hazelnut shells powder lignin
 TBC – Tributyl citrate
 TEC – Triethyl citrate
 WHC – Water holding capacity (%)
 C_{org} – Organic carbon (%)
 LDPE – Low density poly(ethylene)
 T_{cc} – Cold crystallization temperature (°C)
 ΔH_{cc} – Enthalpy of cold crystallization (J g⁻¹)
 ΔH_c – Enthalpy of crystallization (J g⁻¹)

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