

Document downloaded from:

<http://hdl.handle.net/10251/176272>

This paper must be cited as:

Gil-Castell, O.; Andres-Puche, R.; Dominguez, E.; Verdejo, E.; Monreal Mengual, L.; Ribes-Greus, A. (2020). Influence of substrate and temperature on the biodegradation of polyester-based materials: Polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability*. 180:1-16.  
<https://doi.org/10.1016/j.polymdegradstab.2020.109288>



The final publication is available at

<https://doi.org/10.1016/j.polymdegradstab.2020.109288>

Copyright Elsevier

Additional Information

O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288

## **Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases**

O. Gil-Castell<sup>1,2</sup>, R. Andres-Puche<sup>1</sup>, E. Dominguez<sup>3</sup>, E. Verdejo<sup>3</sup>, L. Monreal<sup>1</sup>, A. Ribes-Greus<sup>1,\*</sup>

This is an open-access version, according to <http://v2.sherpa.ac.uk/id/publication/16543>

Full text available at:

<https://www.sciencedirect.com/science/article/pii/S0141391020302202>

DOI:

<https://doi.org/10.1016/j.polymdegradstab.2020.109288>

Please, cite it as:

O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288

<sup>1</sup>Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV).  
Camino de Vera, s/n, 46022 Valencia, Spain.

<sup>2</sup>Departament d'Enginyeria Química. Escola Tècnica Superior d'Enginyeria. Universitat de València. Av. de la Universitat, s/n, 46100 Burjassot, Spain.

<sup>3</sup>AIMPLAS, Gustave Eiffel 4 (València Parc Tecnològic), Paterna, 46980, Spain

\*Corresponding author:

A. Ribes-Greus [aribes@ter.upv.es](mailto:aribes@ter.upv.es)

## **Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases**

O. Gil-Castell<sup>1,2</sup>, R. Andres-Puche<sup>1</sup>, E. Dominguez<sup>3</sup>, E. Verdejo<sup>3</sup>, L. Monreal<sup>1</sup>, A. Ribes-Greus<sup>1,\*</sup>

### **Abstract**

The extended use of polymers from renewable resources such as aliphatic polyesters or polyhydroxyalkanoates boosted the necessity to understand their behaviour in an end-of-life scenario. Although they can be degraded in reasonable shorter times than traditional polymers, understanding the degradation mechanisms under dissimilar conditions will contribute to further developments in this field. This work aimed to study the effect of temperature and substrate in the degradation of polylactide (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) in a simulated laboratory scale to ascertain their contribution, separately or in combination. For this purpose, nine parallel degradation assays were performed by means of the combination of mesophilic (25 °C), thermophilic (58 °C) and hyperthermophilic (80 °C) temperatures with enriched synthetic medium, compost and standardised soil substrates. Although the analysis of the surface morphology, the thermal properties and the thermo-oxidative stability revealed changes as a function of time, the evaluation of the molar mass allowed for a more precise determination of the degradation. In general, chain scission was perceived in all cases as a function of time. The effect of temperature was critical, significantly more important than the effect of the substrate, which showed a less significant contribution, especially in terms of molar mass reduction. While for the PLA, biodegradation at 58 °C and thermal degradation at 80 °C resulted in similar consequences, for the PHBH the hyperthermophilic temperature of 80 °C was the most severe condition, regardless of the substrate. From a technological perspective, it may be highlighted that biodegradation at 58 °C may be the most cost-effective condition due to the lower energy supply required and the valuable contribution of the microorganisms.

### **Keywords**

Biodegradation; biomaterial; polyester; substrate; temperature; PLA; PHBH

## 1. Introduction

Traditional synthetic polymers possess high versatility and low cost, and are widely used in the industrial and domestic sectors. However, they are usually obtained from non-renewable resources and its availability may be subjected to economic and ecologic concerns in a short-term scenario [1]. Although there is increasing social awareness regarding the proper management of plastic waste, a quarter of the total recovered waste in 2018 in Europe still went to landfill, where it can take up to hundreds of years to decompose [2]. Given its intrinsic high resistance to corrosion, water and bacterial decomposition their disposal in terrestrial and marine ecosystems involves a serious environmental problem [3].

The replacement of traditional plastics by biopolymers, including those obtained from renewable resources, may minimize the amount of permanently deposited plastic waste, especially for high-consume applications. For this reason, the use of biomaterials based in aliphatic polyesters as polylactide (PLA) and polyhydroxyalkanoates as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) gained importance in the packaging or agriculture sectors, particularly in North America and Europe [4]. The consideration of cradle-to-cradle approach may result in beneficial industrial systems and positive economic, environmental and social goals would be achieved [5].

In an end-of-life framework, residues of such biopolyesters may have to be managed and valorised. Although recycling has been postulated as a feasible alternative in some cases [6,7], their biodegradation needs to be addressed as a real valorisation route. Both PLA and PHB may undergo degraded in reasonably shorter times than traditional petroleum-based polymers, in the order of hundreds of days or tens of months [3]. In particular, the environmental conditions during the degradation play a determining role, being able to modulate the disintegration and bioassimilation rate of such biopolymers [8]. Therefore, disposal routes must be carefully managed for a satisfactory valorisation and assimilation after their service-life from a cost-effective perspective, energetically affordable and environmentally friendly [9]. In this line, understanding the degradation mechanisms under dissimilar conditions will contribute to further developments in the field of biodegradable plastics [10,11].

During biodegradation depolymerisation reactions occur, in which non-competitive stages deteriorate, erode and disintegrate the polymer. In polyester based materials such as PLA and PHBH, the ester bond is the more labile and probably to shrink site and chain breakage will take place at this point [12]. First, chain scission through hydrolytic breakage happen and then, once reached oligomeric species, chains reintegrated into the carbon cycle by assimilation and mineralisation in the media [13,14]. Several factors may determine the biodegradation kinetics under in-land conditions such as the concentration of the material in the medium or the nature of

the microbial populations, whereas the obtained results might vary significantly depending upon the standard test specifications [15]. Studies dealing with the evaluation of the biodegradation in a laboratory scale are in continuous advance [16]. The biodegradation of PLA and PHAs has been evaluated under a series of standardised conditions (ASTM, EN and ISO), including aerobic and anaerobic or in different substrates such as sewage sludge, compost or soil, as gathered in **Table 1**.

**Table 1.** Biodegradation evaluation studies of PLA and polyhydroxyalkanoates (PHAs) in the literature.

Organisation	Code	Title	Material	
			PLA	PHAs
ASTM	D5209	Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge	[17]	[18,19]
	D5338	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures	[13,20–22]	-
	D5526	Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions	[23]	-
	D5988	Standard test method for determining aerobic biodegradation of plastic materials in soil	[20]	[24–26]
EN	14046	Packaging - Evaluation of the ultimate aerobic biodegradability and disintegration of packaging materials under controlled composting conditions - Method by analysis of released carbon dioxide	-	-
	14806	Packaging - Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test	[27]	-
ISO	14852	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide	[28–30]	[29,30]
	14855	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide	[13,22,38–42,28,31–37]	[43,44]
	16929	Plastics - Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test	-	[44]
	17556	Plastics - Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved	-	[26]
	20200	Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test	[45–54]	[45,46,51]

Although variations of the standardised conditions have been proposed in the literature [54], the contribution of the temperature and substrate on the biodegradation of these materials was not still compared in a simultaneous experiment. Therefore, this work aimed to study the effect of temperature and substrate in the degradation of polylactide (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) in a simulated laboratory scale in order to ascertain the contribution of the different factors in such dissimilar environments. For this purpose, a multiple perspective characterisation methodology was applied and standardised indications were followed. For such evaluation, the Design of Experiments (DoE) was considered as a useful,

O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288

reliable and immediate procedure to elucidate the contribution of time, temperature and substrate on the degradation both individually or in combination [8,55,56]. An analysis of variance was applied in terms of the molar mass and the physico-chemical changes during degradation were evaluated.

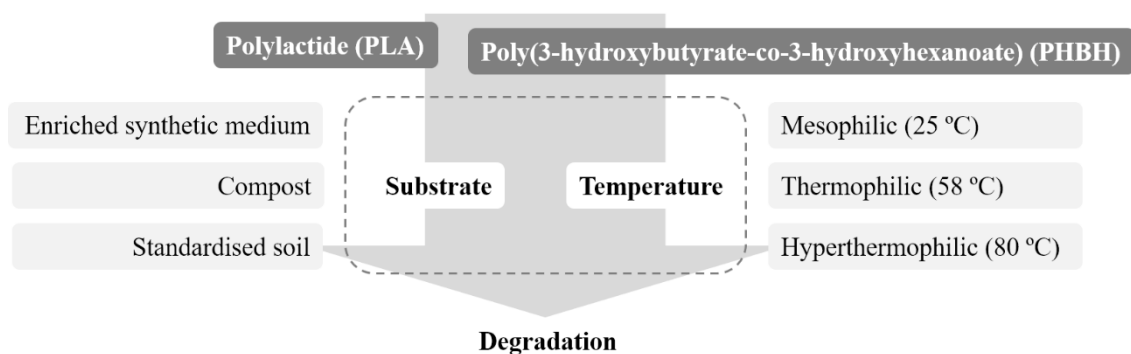
## 2. Materials and methods

### 2.1. Materials and preparation of plates

Polylactide (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) were used as raw materials for the preparation of plates. PLA with a density of  $1.24 \text{ g}\cdot\text{cm}^{-3}$  and a glass transition temperature ( $T_g$ ) in the 60-70 °C range and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) with a density of  $1.25 \text{ g}\cdot\text{cm}^{-3}$  and  $T_g$  in the range from 0 to 5 °C were considered. The molar ratio of 3-hydroxyhexanoate in PHBH was 6%. The preparation of plates was carried out by means of thermo-compression. The pellets of PLA and PHBH were processed in a hot plate press Fontijne Grotnes BV (Model LPC 600) and pressure and temperature of 100 kN and 200 °C, respectively, were applied during 15 min. Plates with dimensions of  $145\times 145 \text{ mm}^2$  were obtained, from which samples were cut with dimensions of  $25\times 25 \text{ mm}^2$ , as defined in the UNE-EN ISO 20200 standard [57]. The thickness of the plates was  $1\pm 0.1 \text{ mm}$ . Finally, the samples were kept in zip bags and placed in desiccators until further analyses.

### 2.2. Degradation assays

The degradation was carried out in standardised conditions, considering as the baseline scenario the indications of the UNE-EN ISO 20200 [57]. However, three different temperatures of incubation were selected: hyperthermophilic temperature of  $80\pm 2 \text{ }^\circ\text{C}$ , thermophilic temperature of  $58\pm 2 \text{ }^\circ\text{C}$  and mesophilic temperature of  $25\pm 2 \text{ }^\circ\text{C}$ . Apart from the enriched synthetic medium suggested in the standard, two complementary degradation substrates were considered: standardised soil and compost. All of them were prepared according to the standards specified in the **Table 2**. The overall approach is represented in **Figure 1**.



**Figure 1.** Schematic approach of the present study: effect of substrate and temperature on the degradation of polylactide (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH).

**Table 2.** Description of components of the enriched synthetic medium, standardised soil and compost.

Materials	Description	Enriched synthetic medium [57]	Compost [58]	Standardised soil [59]
		Dry mass composition (%)		
Compost	Organic origin of pruning remains	10	100	4
Sawdust	From untreated wood	40	-	-
Rabbi food	Alfalfa based commercial product	30	-	-
Saccharose	Powder	5	-	-
Corn-starch	Powder	10	-	-
Corn oil	Density 0.9 g·ml <sup>-1</sup> at 25 °C	4	-	-
Urea	Powder	1	-	-
Sand	Fine industrial quartz sand (0.2 mm)	-	-	70
Clay	Red clay (kaolin)	-	-	10
Natural Soil	Obtained from the area	-	-	16
KH <sub>2</sub> PO <sub>4</sub>	Powder	-	-	0.2
MgSO <sub>4</sub>	Powder	-	-	0.1
NaNO <sub>3</sub>	Powder	-	-	0.4
NH <sub>4</sub> Cl	Powder	-	-	0.4
Urea	Powder	-	-	0.2

For the degradation analyses, the samples were mixed with the substrates so that they were perfectly buried. Given the mass ratio of the sample/substrate specified in the standard, a concentration of 5 g polymer per 1000 g of substrate (dry weight) was considered. The bioreactors were polypropylene containers with dimensions of 30×20×10 cm<sup>3</sup>, and plugged to avoid excessive evaporation. At the centre of the sides and approximately at 6.5 cm of height, holes of 5 mm diameter facilitated the exchange of gases between the inner and the outer environment. Once mixed the polymer samples and substrates, the bioreactors were closed, weighed and placed in a Memmert ICH750L climate chamber. In order to ensure adequate environmental and humidity conditions, aeration of the substrates was performed and humidity was periodically monitored and maintained between the limits.

The samples were extracted and washed in triplicates after 15, 60 and 90 days of degradation. In the last stage, the substrates were sieved (2 mm) in order to recover remnant sample fragments. In all the cases, the samples were dried at 40±2 °C into a vacuum oven until a constant mass was reached and furtherly stored for subsequent analyses. The degree of disintegration (*D*), was calculated according to the **Equation 1**:

$$D (\%) = \frac{m_i - m_r}{m_i} \times 100 \quad \text{Equation 1}$$

where  $m_i$  is the initial dry mass and  $m_r$  is the dry mass of the residual sample recovered from the sieve.

### 2.3. *Physico-chemical characterisation*

#### 2.3.1. *Size Exclusion Chromatography (SEC)*

Size exclusion chromatography (SEC) was performed on different devices, given the dissimilar solubility of PLA and PHBH. Tetrahydrofuran (THF), ( $\geq 99.8\%$ ) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were used as solvents for the PLA and PHBH, respectively, and were supplied by Sigma-Aldrich® and used without further purification.

For the PLA, analyses were carried out by means of a Malvern Instruments Omnisec Resolve chromatograph. It combined an integrated pump, a degasser, an autosampler and a column oven, along with a Malvern Instruments Omnisec Reveal multi-detector –Ultraviolet (UV), Refractive Index (RI), Low and Right-Angle Light Scattering (LALS and RALS) and Viscosity (VISC). A standard sample of monodispersed polystyrene with a  $dn/dc$  value of 0.185 was used to calibrate the equipment. Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of  $1 \text{ mL} \cdot \text{min}^{-1}$  and a column temperature of  $35 \text{ }^\circ\text{C}$ . Two Malvern Instruments columns (T2000 and T4000) were used. The samples were dissolved in THF at concentrations of approximately  $2 \text{ mg} \cdot \text{mL}^{-1}$  and then filtered through PTFE filters of  $0.45 \text{ } \mu\text{m}$ . Three injections were performed per sample and the data obtained were analysed using the OMNISEC V10™ software.

For the PHBH, analyses were carried out by means of an Agilent Infinity 1260 chromatograph. Separation was performed with a Jordi Associates mixed bed fluorinated column with permeation range  $100\text{--}10 \times 10^6$  Dalton. All the samples were dissolved in HFIP, which was also used as mobile phase containing  $2.72 \text{ g} \cdot \text{L}^{-1}$  of sodium trifluoroacetate (NaTFA). This solvent was previously degassed by vacuum filtration over PTFE  $0.45 \text{ } \mu\text{m}$  pore membranes. The flow rate was  $1 \text{ mL} \cdot \text{min}^{-1}$  and temperature was set at  $35 \text{ }^\circ\text{C}$ . Detection was conducted by UV-vis-detector. Monodisperse polymethylmethacrylate patterns from Sigma Aldrich were used for the calibration.

#### 2.3.2. *Field Emission Scanning Electron Microscopy (FE-SEM)*

The surface morphology of the samples was analysed by means of a Zeiss Ultra 55 field emission scanning electron microscope (FE-SEM). The samples were cut into small pieces and mounted on metal studs and sputter-coated with a platinum layer during 15 s using a Leica EM MED020. Analyses were carried out at room temperature with a 1 kV voltage.

#### 2.3.3. *Thermogravimetric Analysis (TGA)*

The thermo-oxidative stability was assessed by means of thermogravimetric analysis (TGA) in a Mettler-Toledo TGA 851 series. The samples, with a mass of about 4 mg, were introduced into  $70 \text{ } \mu\text{L}$  Mettler-Toledo perforated alumina crucibles. A dynamic method was considered with a



O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288

heating rate of 10 °C·min<sup>-1</sup> from 25 to 800 °C in an oxygen atmosphere. The samples were analysed in triplicates and averages and deviations were taken as representative.

#### 2.3.4. Differential Scanning Calorimetry (DSC)

The thermal properties were analysed by means of differential scanning calorimetry (DSC) in a Mettler-Toledo DSC 820e device. The samples with a mass of 4 mg, were deposited in perforated aluminium crucibles of 40 µl. Analyses were carried out the range from 0 °C to 200 °C with a heating rate of 10 °C·min<sup>-1</sup> under inert atmosphere of N<sub>2</sub>. The samples were analysed in triplicates and averages and deviations were taken as representative. The crystallinity degree ( $X_c$ ) of the plates was calculated by means of the **Equation 2**:

$$X_c(\%) = \frac{\Delta h_m - \Delta h_{cc}}{\Delta h_m^0} \times 100 \quad \text{(Equation 2)}$$

Where  $\Delta h_m$  and  $\Delta h_{cc}$  are the measured melting enthalpy and cold crystallisation enthalpy and  $\Delta h_m^0$  is the heat of fusion of 100% crystalline PLA and PHB with values of 93 and 146 J·g<sup>-1</sup>, respectively [60,61].

#### 2.4. Factorial statistical study

Statistical Design of Experiments (DoE) was performed with the Minitab® 19.2 software. The effect of the time, temperature and substrate on the biodegradation of PLA and PHBH were assessed by means of the analysis of variance. The average molar mass in number ( $M_n$ ) was selected as a key indicator of the chain scission during degradation. As a result, main effect plots (MEF) and interaction plots (IP) were obtained.

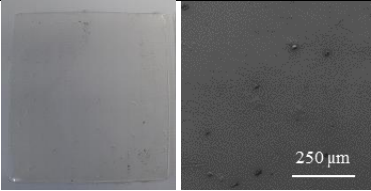
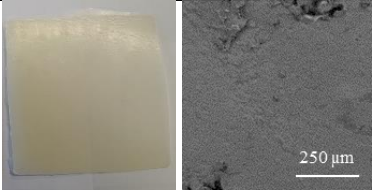
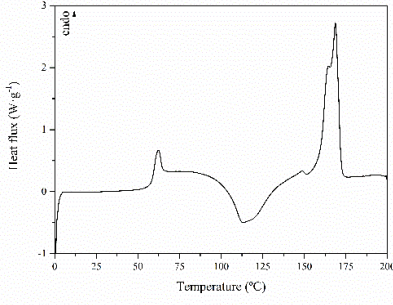
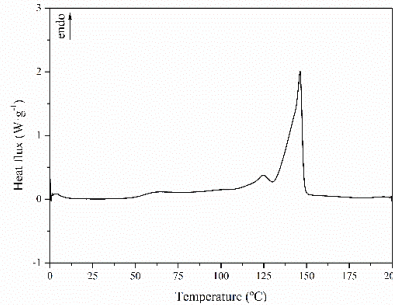
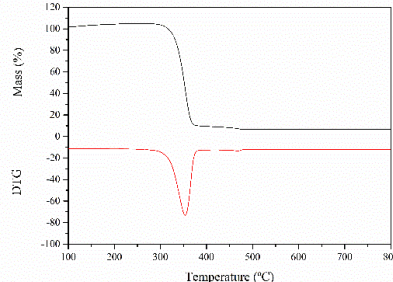
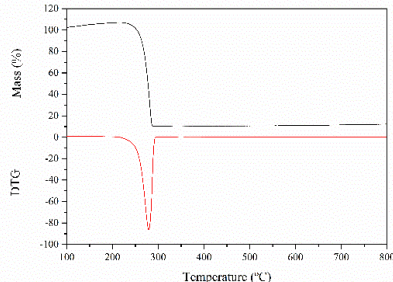
### 3. Results and discussion

The native PLA and PHBH plates were physico-chemically characterised in order to establish the baseline for further characterisations. Next, the degradability of the PLA and PHBH was evaluated in terms of disintegration degree after 90 days in the different substrates and temperatures. Then, the changes underwent in the different conditions were assessed as a function of the degradation time in different stages: 0, 15, 60 and 90 days. The molar mass was considered as the main degradation indicator, and the influence of the time, substrate and temperature were statistically analysed. Subsequently, the changes in the physico-chemical properties of the plates were evaluated following a multiple approach in which the macroscopic appearance of the samples, the microscopic surface, the thermo-oxidative stability, the thermal properties and crystallinity were evaluated.

### 3.1. Physico-chemical characterisation of initial PLA and PHBH

The molar mass, the macro and microscopic morphology, the thermal properties and the thermo-oxidative behaviour of the prepared PLA and PHBH plates were assessed, which results are gathered in **Table 3**.

**Table 3.** Initial properties of the PLA (left) and PHBH (right) in terms of molar mass, macro and microscopic (100×) morphology, thermal properties and thermo-oxidative stability.

	PLA	PHBH
<b>Molar mass</b>	$M_n = 57000 \text{ g}\cdot\text{mol}^{-1}$ $M_w = 94000 \text{ g}\cdot\text{mol}^{-1}$ $PDI = 1.64$	$M_n = 122000 \text{ g}\cdot\text{mol}^{-1}$ $M_w = 241000 \text{ g}\cdot\text{mol}^{-1}$ $PDI = 2.56$
<b>Macro and microscopic morphology</b>		
<b>Thermal properties</b>		
<b>Thermal stability</b>		

The plates of PLA were translucent with uniform thickness around 1 mm and a smooth surface, as corroborated by electron micrographs. The average molar mass in number ( $M_n$ ) was close to  $60000 \text{ g}\cdot\text{mol}^{-1}$ , according to the manufacturer specifications, and a polydispersity index ( $PDI$ ) of 1.64 was found. The PLA showed the consecutive processes of the glass transition ( $T_g$ ) at  $62 \text{ }^\circ\text{C}$ , the cold-crystallisation ( $T_{cc}$ ) at  $113 \text{ }^\circ\text{C}$  and the melting ( $T_m$ ) at  $168 \text{ }^\circ\text{C}$  [62]. A crystallinity degree ( $X_c$ ) of 16.97% was calculated. In terms of thermo-oxidative-stability, the PLA plates were decomposed in a single stage with a peak temperature ( $T_d$ ) at  $354 \text{ }^\circ\text{C}$  [63,64].

The plates of PHBH were yellowish and opaque with a thickness around 1 mm. The average molar mass in number ( $M_n$ ) was  $122000 \text{ g}\cdot\text{mol}^{-1}$ . It is important to remark the relatively high

polydispersity index (*PDI*) of 2.56, characteristic of the biological synthesis of the PHBH with wide multimodal molar mass distributions [65]. The surface was apparently smooth. However, microscopic analyses revealed a slight roughness, due to the mould marks during thermo-compression processing. A semicrystalline structure was found, with a glass transition temperature ( $T_g$ ) at 3 °C, a main melting peak ( $T_m$ ) at 146 °C and a small melting shoulder at 124 °C with an overall crystallinity degree ( $X_c$ ) of 27% [66,67]. The PHBH plates revealed a one stage thermo-oxidative decomposition, which peak temperature ( $T_d$ ) was 279 °C.

Although both PLA and PHBH are bio-based polyesters, their dissimilar physico-chemical properties may offer a good reference point to evaluate the effect of the temperature and substrate on the degradation of such materials.

### 3.2. Degradability in standardised conditions

The PLA and PHBH degradability were evaluated in terms of the disintegration degree (*D*) as the remaining percentage of the samples at the end of the assay, according to the above described **Equation 1**. The obtained *D* values after 90 days are gathered in **Table 4** for the PLA and PHBH subjected to degradation in the different substrates and temperatures.

**Table 4.** Average disintegration degree (*D*) of the PLA (left) and PHBH (right) after 90 days of degradation in the different substrates and temperatures.

		Substrate	Temperature (°C)		
			25 °C	58 °C	80 °C
PLA	Synthetic	2.15 ± 0.52	100.00	100.00	
	Compost	0.24 ± 0.21	100.00	100.00	
	Soil	2.32 ± 0.67	100.00	100.00	
PHBH	Synthetic	1.69 ± 0.28	41.03 ± 3.44	8.89 ± 2.55	
	Compost	0.53 ± 0.31	25.08 ± 6.22	13.04 ± 4.22	
	Soil	2.52 ± 0.75	9.60 ± 1.98	7.23 ± 2.30	

For the PLA plates, the mesophilic temperature of 25 °C resulted in low disintegration, below 3% regardless of the substrate. At the thermophilic temperature of 58 °C, the disintegration was complete for the synthetic, compost and soil substrates [35,68]. The hyperthermophilic temperature of 80 °C also caused complete disintegration in all the substrates. Given the disappearance of the samples and subsequent assimilation after 90 days of burial at 58 and 80 °C, the particular effect of the substrate and temperature on the disintegration procedure could not be clearly ascertained in the PLA plates.

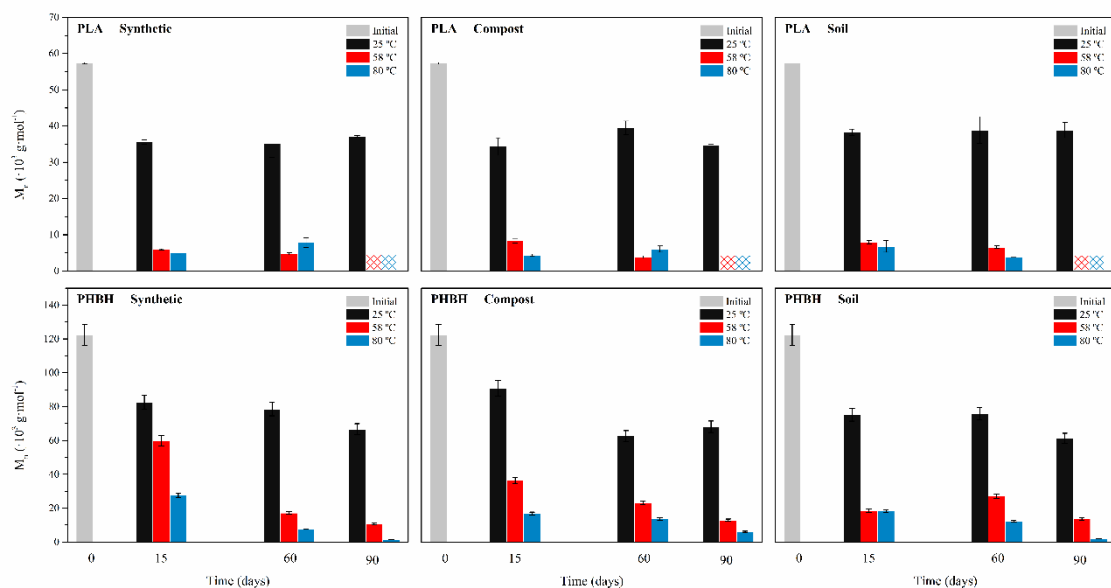
The disintegration of the PHBH revealed a slightly different behaviour. At the mesophilic temperature of 25 °C similar results to that of PLA were perceived with disintegration below 3% in all the substrates. However, the thermophilic temperature of 58 °C revealed disintegration around 41% in the synthetic substrate, 25% in compost and 9% in soil. Finally, the

hyperthermophilic temperature of 80 °C provoked a disintegration degree in the compost of 13%, whilst similar disintegration was found in the synthetic and soil substrates around 8%. According to the disintegration results, the thermophilic temperature of 58 °C in the synthetic substrate was the most degrading circumstance. Under these conditions, the biodegradation of the PHBH resulted in the highest disintegration degree.

### 3.3. Degradation evaluation: molar mass

The molar mass of the PLA and PHBH plates in the different substrates and temperatures was evaluated as a function of the degradation time and was selected as the key indicator of the degradation. This analysis precisely determine the occurrence and allows quantification of the degradation by means of the polymer segment size evaluation [54,69,70]. For this purpose, size exclusion chromatography (SEC) analyses were carried out and the chain scission occurred during degradation was evaluated by means of the average molar mass in number ( $M_n$ ), which results are plotted in **Figure 2**. In general, the molar mass diminished as a function of time both for the PLA and PHBH in all the substrates and temperatures. In particular, a large diminution was observed in the first stage of immersion, which is characteristic for the degradation in bulk of both selected polyester-based materials [10]. Chain scission occurs rapidly in the first stage of degradation given the humidity and temperature contribution, which hydrolyses the ester linkages. During this period, especially the degradation of the amorphous fraction occurs. Then, the erosion and fragmentation take place. The integrity of the sample after long time degradation is given by the crystalline fraction of the sample, which will be evaluated in next sections.

The degradation in the different substrates revealed a similar behaviour. However, slightly diverse tendencies were found, furtherly evaluated in detail.



**Figure 2.** Average molar mass in number ( $M_n$ ) for the PLA (up) and PHBH (down) as a function of the degradation time for the different substrates and temperatures.

For the PLA, the mesophilic temperature of 25 °C promoted a moderate decrease of molar mass of near 40% from 57000 g·mol<sup>-1</sup> to values close to 35000 g·mol<sup>-1</sup> regardless of the substrate. The thermophilic and hyperthermophilic temperatures of 58 and 80 °C, respectively, promoted a similar behaviour, in which molar mass dramatically decreased from the first stage of burial [54,62]. A reduction of around 90% of the initial molar mass was found after day 15 in all the substrates, and values between 10000 and 5000 g·mol<sup>-1</sup> were reached. It is important to remark that most of the degradation occurred before day 15 of the trial. That is, from this point onwards the molar mass remained almost constant until disintegration. This behaviour is characteristic of PLA-based materials subjected to biodegradation above its glass transition temperature [71], and is boosted due to the higher activity of water molecules as compared to the equilibrium state [42,72,73].

For the PHBH, the mesophilic temperature of 25 °C promoted a decrease of around 30% of molar mass, moving from 122000 g·mol<sup>-1</sup> to 80000 g·mol<sup>-1</sup> in all the substrates. However, at the thermophilic temperature of 58 °C the molar mass variation revealed diverse tendencies for the different substrates. In the enriched synthetic medium, a progressive reduction was observed as a function of time, following a moderate decreasing exponential function. Then, in the compost and soil, slightly higher degradation in the first stage was found, which values around 30000 g·mol<sup>-1</sup> remained almost constant until the end of the assay. Finally, the hyperthermophilic temperature of 80 °C was the most severe degradation condition, with a decrease of more than 90% of molar mass after day 90 regardless of the substrate.

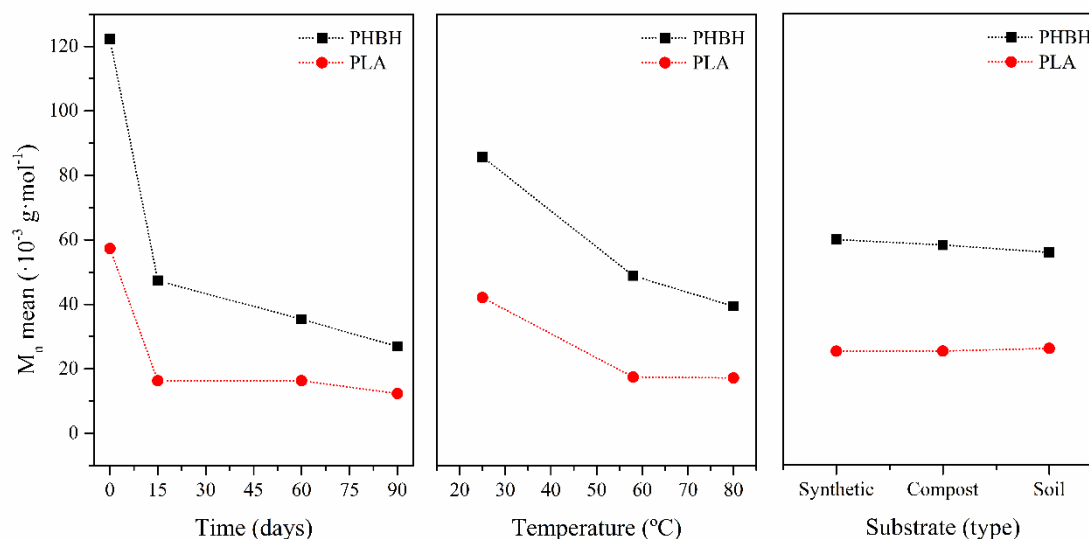
In order to furtherly evaluate the effect of the substrate and temperature on the degradation of the PLA and PHBH plates through the molar mass variation, a factorial approach was carried out in the next section. The contribution of both factors on the  $M_n$  was therefore assessed and discussed.

### *3.3.1. Multiple degradation approach: individual and combined effect of substrate and temperature on the molar mass of PLA and PHBH*

As a consequence of the multiple factors considered in this study, it may be difficult to elucidate the contribution of time, temperature and substrate on the degradation of PLA and PHBH. When they are applied simultaneously, their influence may be boosted, overlapped or even buffered. Given the big number of combined conditions, the evaluation of the individual contribution and the combination of factors may be crucial to understand the degradation of such polyester-based materials. In order to overcome these limitations a factorial statistical study was carried out. For this purpose, an analysis of variance was applied to the obtained results in terms of the average molar mass in number ( $M_n$ ). As a result, the main effects (MEP) and interaction (IP) plots were

obtained, which are very useful and intuitive tools to ascertain the influence of different factors, separately or in combination, on the response of a given process [8,56,74].

The main effect plots (MEP) of the time, substrate and temperature on the mean of the average molar mass in number ( $M_n$ -mean) of PLA and PHBH are represented in **Figure 3**. Considering the differences in the absolute values of the  $M_n$ -mean, a similar behaviour was found for both materials. However, some particularities may be highlighted.

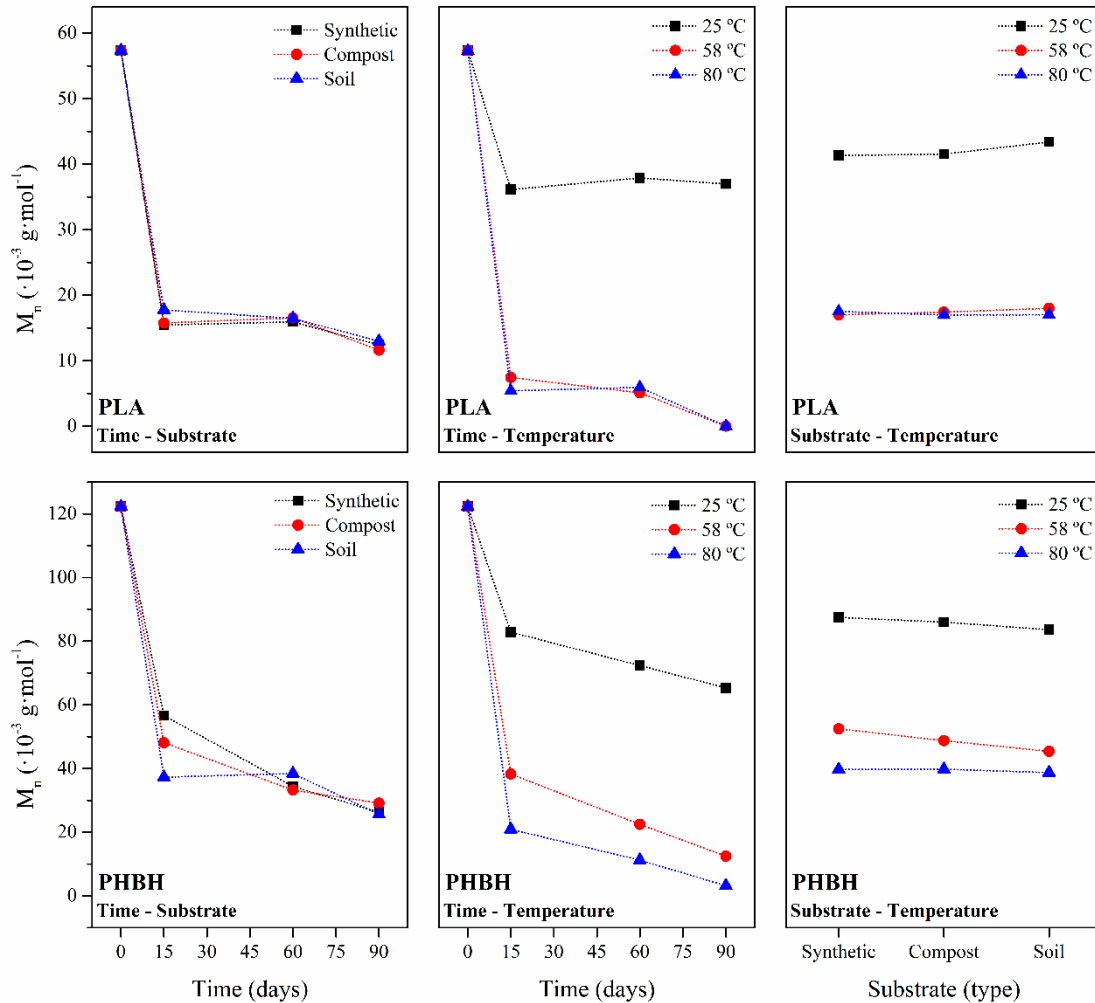


**Figure 3.** Main effect plots of the time (left); substrate (middle); and temperature (right) on the average molar mass in number mean ( $M_n$  mean) in the degradation of PLA and PHBH.

In the PLA, significant degradation occurred after 15 days, and the increase of time did not furtherly reduced molar mass. Moreover, the increase in the temperature resulted in greater degradation. The mesophilic temperature of 25 °C promoted moderate changes in the molar mass, while the thermophilic of 58 °C and hyperthermophilic of 80 °C resulted in higher and similar molar mass reduction. Finally, the effect of the substrate was not relevant on the  $M_n$ -mean. The synthetic, compost and soil substrates caused similar degradation regardless of the time and temperature.

For the PHBH, in terms of time, the first 15 days were the critical stage, where the molar mass considerably decreased. However, while in PLA the molar mass barely changed in further extractions, the degradation of PHBH progressively continued as the time increased. A similar tendency occurred with the effect of temperature. The increase in the temperature significantly promoted degradation and, in this case, the most severe conditions were the hyperthermophilic temperature of 80 °C, followed by the thermophilic temperature of 58 °C and finally the mesophilic temperature of 25 °C. As found before for PLA, the differences in terms of the  $M_n$ -mean between the studied substrates were non-significant.

At this point, the combination of time, temperature and the different substrates was evaluated. Factors such as the temperature, along with the substrate characteristics and the presence of microorganisms and/or humidity may result in a synergistic behaviour. Accordingly, biodegradation, hydrothermal degradation or thermal degradation may prevail in the different conditions [54]. Therefore, the interaction plots (IP) were obtained, which are represented in **Figure 4** for the PLA and PHBH, respectively.



**Figure 4.** Interaction plots (IP) of the time-substrate (left); time-temperature (middle); and substrate-temperature (right) on the average molar mass in number ( $M_n$ ) in the degradation of PLA (up) and PHBH (down).

For the PLA, non-significant differences were found as a function of time in the different substrates. Then, when combined time and temperature, 25 °C resulted in considerably lower degradation than 58 and 80 °C, which revealed almost identical results. Finally, when the effect of substrate and temperature were combined, the above-mentioned significant contribution of temperature was found, while the effect of the substrate was virtually negligible.

For the PHBH, the consequence of the increase of time was similar in the different substrates. Slightly higher degradation was found in the soil substrate in the first stage of the assay, followed by the compost and synthetic substrates. Then, higher temperatures increased degradation as a function of time. The degradation at 25 °C was less substantial than that of 58 and 80 °C, respectively. In this case, the hyperthermophilic temperature was the most aggressive condition. Finally, when combined substrate and temperature, this observation could also be perceived, while non-representative contribution of the substrate was found.

As a general overview, omitting the slight differences between the PLA and PHBH, the temperature was the crucial factor on the  $M_n$  reduction. On the one hand, higher temperatures enhanced both polymer chain mobility and water molecules activity, that resulted in advanced hydrolysis of the polymers by means of the ester bond breakage. On the other hand, given the analogous degradation pattern found at the thermophilic and hyperthermophilic temperatures, the contribution of microorganisms at 58 °C seemed to have compensated the higher temperature of 80 °C in order to achieve comparable degradation consequences in terms of molar mass reduction.

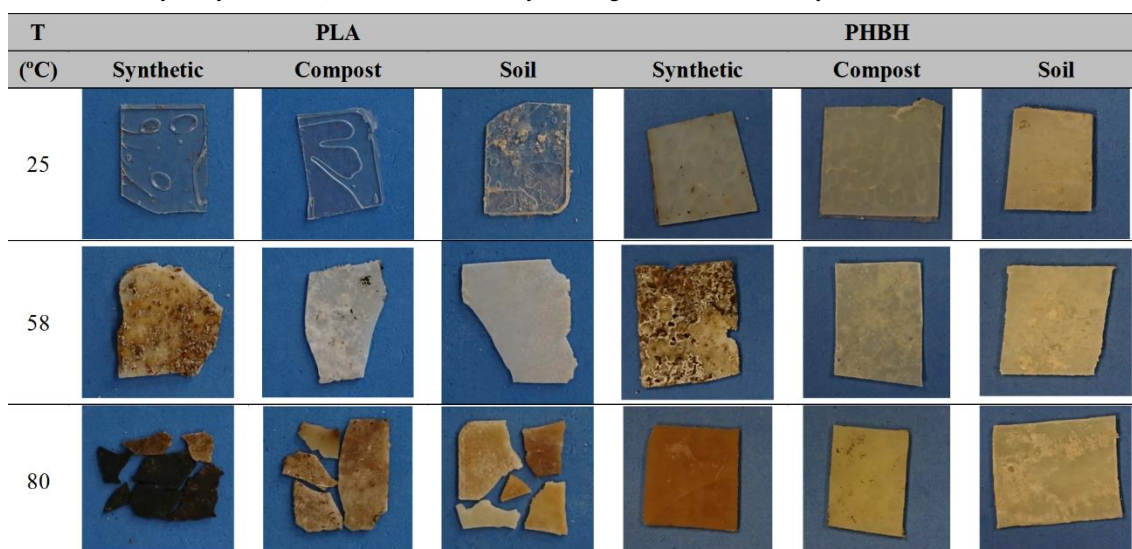
#### *3.4. Changes during degradation*

As a complementary analysis to the chain scission evaluation, the effect of the substrate and temperature, on the physico-chemical properties of the PLA and PHBH plates during degradation were monitored and evaluated. For this purpose, the macroscopic and microscopic appearance as well as the crystallinity and thermo-oxidative stability were analysed as a function of the degradation time.

##### *3.4.1. Macroscopic appearance*

The evaluation of the macroscopic appearance during degradation may give an overview of the changes underwent in the PLA and PHBH plates. The overall outline of the macroscopic variations during burial in all the conditions is shown in **Tables S1** and **S2** in the Supplementary Material. In general, the macroscopic appearance changed as a function of time. The loss of transparency, the change of colour, the increase in the surface roughness, the erosion and fragmentation and the development of biodegradation spots were perceived [12]. However, diverse patterns were observed in the different conditions. For comparison purposes, the macroscopic state of the washed samples after 60 days of degradation is shown in **Figure 5**. This period was selected due to the still existence of PLA and PHBH specimens in all the temperatures and substrates.





**Figure 5.** Surface macroscopic appearance of the PLA (left) and PHBH (right) after 60 days of degradation for the different substrates and temperatures.

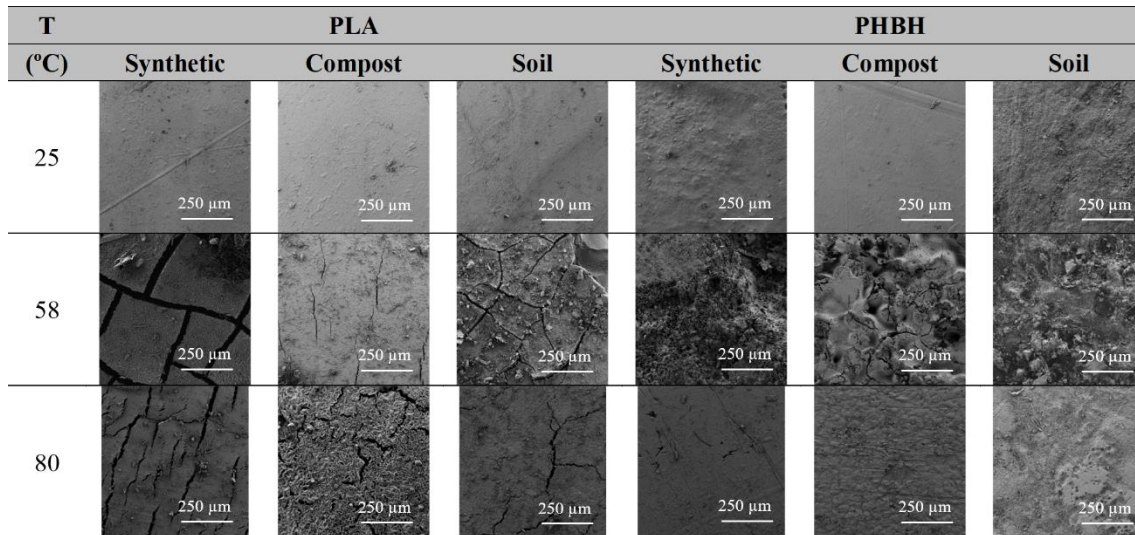
On the one hand, the PLA plates remained almost transparent at 25 °C. Only in the soil substrate a slight change to a yellowish colour with small spots was found, that seemed to be the incipient sites of degradation. At the thermophilic temperature of 58 °C, biodegradation occurred in the synthetic substrate, as identified by the brownish colour and clearly recognised degradation spots. In the compost and soil substrates, the PLA turned opaque and whitish, due to the presumable chain rearrangement and polymer crystallisation caused by humidity and temperature. Finally, at the hyperthermophilic temperature of 80 °C, the PLA turned opaque, acquired a brownish colour and samples were more fragile. The prevalence of thermal degradation may have caused this behaviour [75].

On the other hand, the PHBH maintained the original yellowish colour at the mesophilic temperature of 25 °C in all the substrates. At the thermophilic temperature of 58 °C in the synthetic substrate the main biodegradation characteristics could be observed. Microorganisms had biodegraded the sample locally, as suggested by the presence of dark small spots and the generation of holes in the plate [76]. However, in the compost and soil substrates, the macroscopic state of the PHBH remained unaltered. At the hyperthermophilic temperature of 80 °C, whereas the brownish colour turned more intense in the plates of the synthetic substrate, the PHBH in the compost and soil seemed again unaffected. In this line, it was highlighted the superior stability of the PHBH to the manifestation of macroscopic changes.

Once evaluated an overall picture of the state of the PLA and PHBH plates during degradation for the different substrates and temperatures, the causes and mechanisms of the observed differences were furtherly ascertained.

### 3.4.2. Surface microscopic morphology

The changes in the microscopic scale were evaluated in the surface of the plates by means of field emission scanning electron microscopy (FE-SEM), which obtained images are gathered in **Figure 6**. As for the macroscopic appearance, samples after 60 days of degradation were selected to give a general overview of the process.



**Figure 6.** Surface microscopic morphology (100×) the PLA (left) and PHBH (right) after 60 days of degradation for the different substrates and temperatures (scale bar 250 μm).

As perceived in the previous section, the exposure to the synthetic, compost and soil substrates at the mesophilic temperature of 25 °C did not alter the surface microscopic morphology, both in the PLA and PHBH plates.

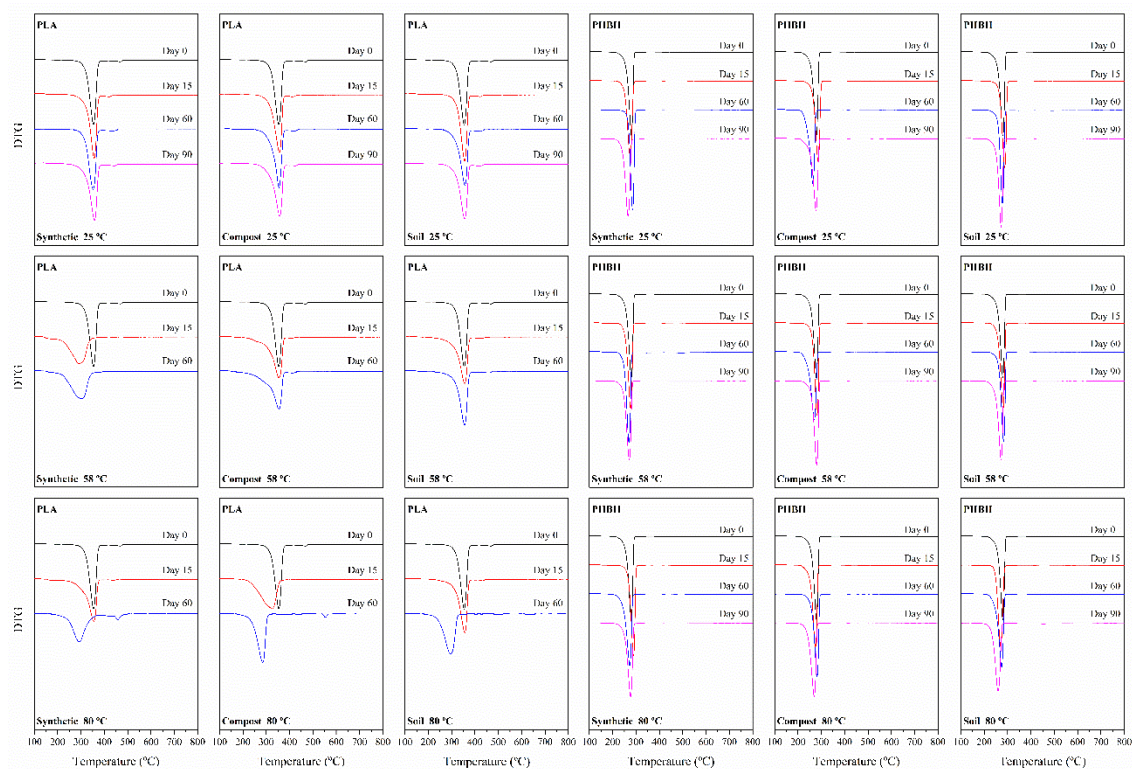
At the thermophilic temperature of 58 °C significant changes were observed for the PLA. Fragmentation due to the apparition of cracks was found, especially perceivable for the synthetic substrate, with an average width of around 35 μm. The compost and soil substrates also promoted cracking but they were not critical. Similar consequences were found at the hyperthermophilic temperature of 80 °C. The surface of the plates revealed widespread cracks of approximately 25 μm of width. The cracking behaviour in the PLA plates has been reported in the literature during bio- and hydrothermal degradation, and may provide alternative paths for water and microorganisms to diffuse, enhancing the consequences of degradation [54,77].

For the PHBH, the thermophilic temperature of 58 °C significantly increased rugosity of the surface regardless of the substrate. Small holes of 35 μm of diameter were found, along with small cracks. These changes point out the colonization of the plate surface by the degrading microorganisms [12]. Finally, the hyperthermophilic temperature of 80 °C did not significantly altered the surface of the PHBH plates. The original flatness of the PHBH plates remained virtually unaffected.

Overall, the PLA and PHBH revealed slightly different degradation mechanisms according to the microscopic appearance. Whilst cracking and fragmentation occurred in the PLA plates, the degradation of PHBH samples was revealed in small holes, which resulted in an increase of the surface porosity.

### 3.4.3. Thermo-oxidative stability

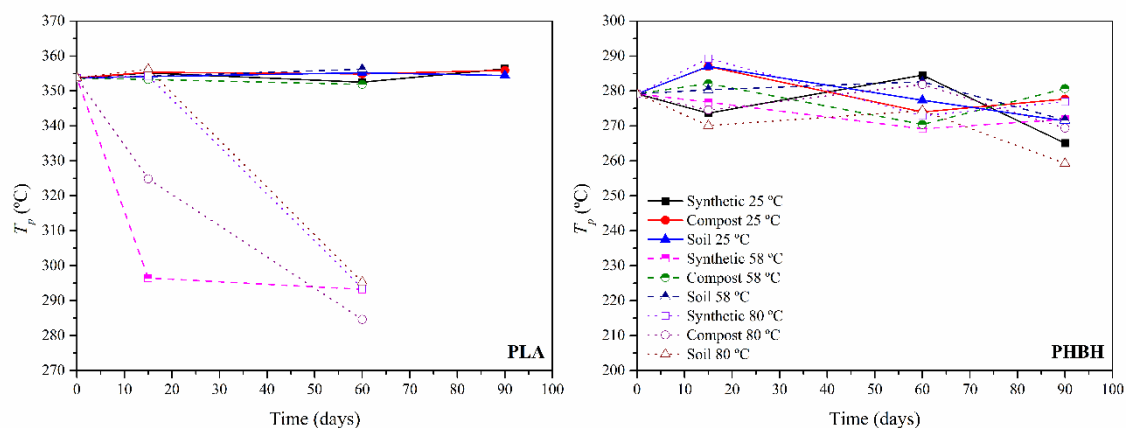
The evaluation of thermo-oxidative stability is a key indicator of degradation in biopolymers and it was therefore evaluated by means of thermogravimetric analysis under oxidative atmosphere [78]. For this purpose, experiments were carried out as a function of the degradation time in the different substrates and temperatures. The obtained derivative-thermogravimetric curves are plotted in **Figure 7** for the PLA and PHBH. The mass percentage ( $\Delta m$ ) and peak temperature ( $T_p$ ) values of the main thermo-oxidative decomposition stage of the PLA and PHBH are gathered in **Table S3** in the Supplementary Material. Moreover, as a key indicator of thermo-oxidative stability, the evolution of the peak temperature ( $T_p$ ) of the DTG curve was selected and plotted as a function of time in **Figure 8**.



**Figure 7.** Derivative TGA curves (DTGA) of the PLA (left) and PHBH (right) as a function of the degradation time for the different substrates and temperatures.

In general, the thermogravimetric curves for PLA showed the mass loss in a single stage in the temperature range between 270 °C and 450 °C. During this stage, the decomposition of the polymer backbone takes place, with a similar total mass loss in all the samples above 90%.

Although the specimens were rinsed after the extraction from the substrate, the residue found in the thermogravimetric analysis as non-decomposed material may correspond to inorganic components, such as precipitated salts. The initial PLA showed a  $T_p$  around 353 °C. Once exposed to the mesophilic temperature of 25 °C any significant alterations in the stability were perceived in none of the three substrates. Although molar mass analyses revealed the existence of degradation, this behaviour is in line with the microscopic and macroscopic appearance observations. For the thermophilic temperature of 58 °C,  $T_p$  remained constant until the plates were fully disintegrated in the compost and soil substrates. However, in the synthetic substrate,  $T_p$  significantly decreased up to values around 300 °C in day 15 and remained close to this value until disintegration. Finally, at the hyperthermophilic temperature of 80 °C, a large decrease of the  $T_p$  was observed, reaching values around 300 °C in day 60 in all the substrates. Afterwards, the PLA collapsed and was completely disintegrated, so thermo-gravimetric analyses could no longer be carried out. Although the hyperthermophilic temperature of 80 °C resulted in a large decrease in the thermo-oxidative stability and, ultimately, in the disintegration of the sample, the great advance of degradation in the synthetic substrate at 58 °C must be highlighted.



**Figure 8.** Degradation peak temperature ( $T_p$ ) for the PLA (left) and PHBH (right) as a function of the degradation time for the different substrates and temperatures. Error bars were omitted for the sake of clarity.

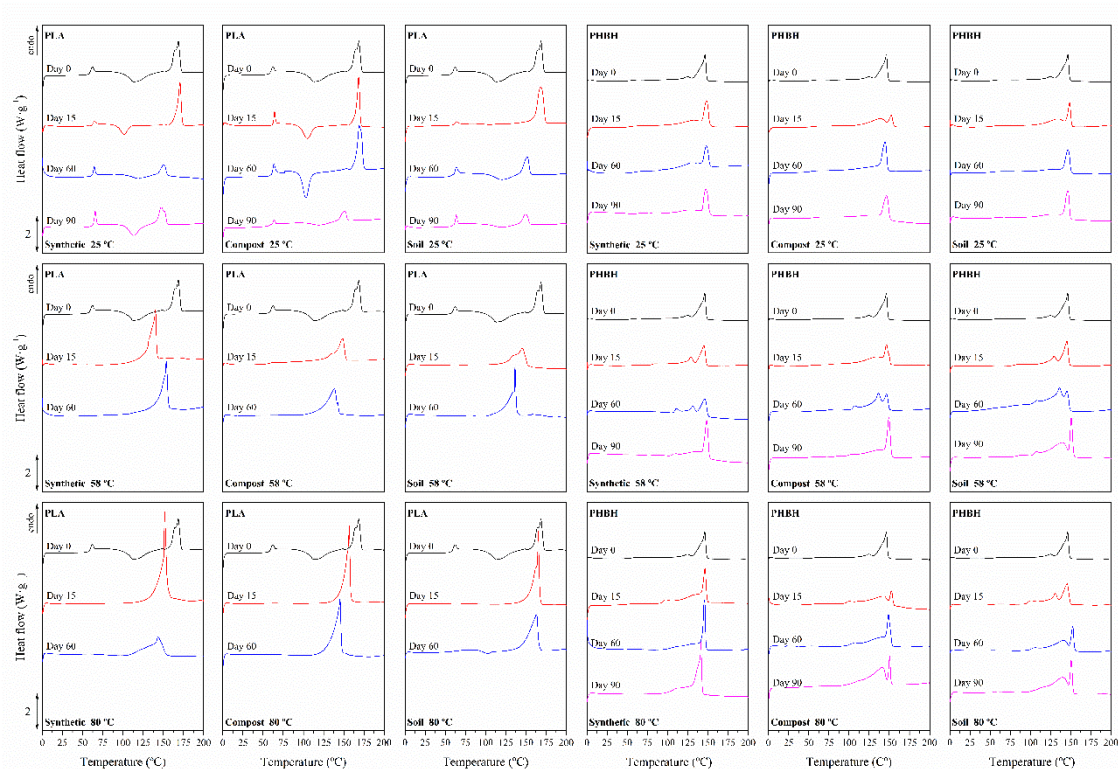
The thermogravimetric curves of the PHBH were similar to those of PLA, in which the mass loss occurred in a single stage, in the temperature range between 250 °C and 300 °C. The mass loss was in all cases greater than 92%. As mentioned above, the remaining percentage could correspond to salts and residue of the substrate embedded in the material. In general, the peak of the derivative thermogravimetric curves slightly moved towards lower temperatures from 279 °C to ~260 °C as the degradation time progressed in the most severe conditions. However, the  $T_p$  values fluctuated in the  $\pm 10$  °C range and, therefore, the effect of the temperature and the substrate could not be clearly evaluated by means of the thermo-oxidative stability analyses. Again,



although degradation was certified by molar mass results, the PHBH virtually kept their thermo-oxidative stability after being subjected to degradation in all the conditions.

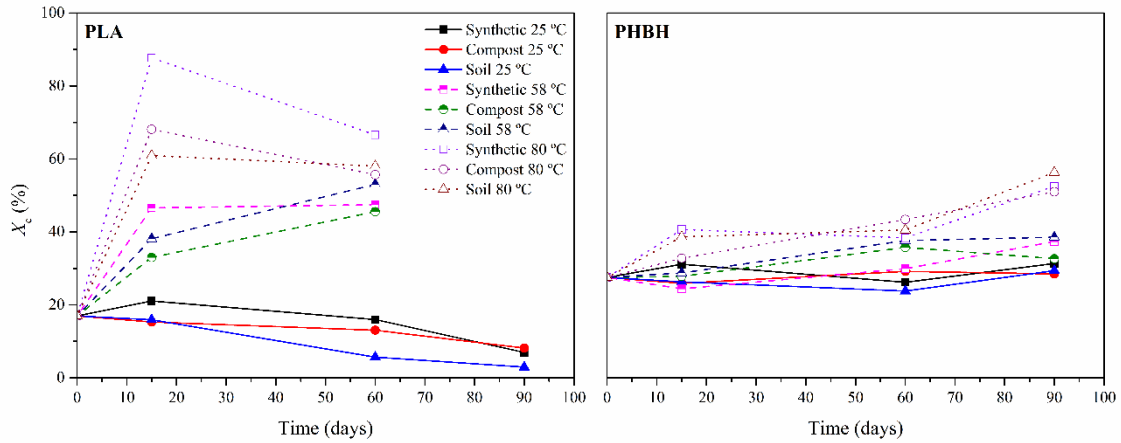
### 3.4.4. Thermal properties

The thermal properties of the PLA and PHBH plates were evaluated in the different substrates and temperatures, as a function of the degradation time. This evaluation is especially relevant for semicrystalline polymers to determine its performance during degradation [64,79,80]. The obtained calorimetric thermograms are plotted in **Figure 9**.



**Figure 9.** DSC thermograms of the first heating scan of the PLA (left) and PHBH (right) as a function of the degradation time for the different substrates and temperatures.

The significant parameters obtained from the thermograms are gathered in the Supplementary Material in **Table S4**. For the PLA the temperature and enthalpy of structural relaxation ( $T_{rl}$ ,  $\Delta h_{rl}$ ), the temperature and enthalpy of cold crystallization ( $T_{cc}$ ,  $\Delta h_{cc}$ ), the melting temperature and enthalpy ( $T_m$ ,  $\Delta h_m$ ) and the degree of crystallinity ( $X_c$ ) were obtained. For the PHBH, the melting temperature and enthalpy ( $T_m$ ,  $\Delta h_m$ ) and the degree of crystallinity ( $X_c$ ) were calculated. In particular, the variation of  $X_c$  was considered as the most relevant indicator of the degradation, which may give valuable information of the change in the microstructure of the plates. The evolution of  $X_c$  as a function of time is plotted in **Figure 10** for the different conditions.



**Figure 10.** Crystallinity degree ( $X_c$ ) for the PLA (left) and PHBH (right) as a function of the degradation time for the different substrates and temperatures. Error bars were omitted for the sake of clarity.

At the mesophilic temperature of 25 °C, the structural relaxation increased its enthalpy ( $\Delta h_{rl}$ ) and temperature ( $T_{rl}$ ) as a function of time regardless of the substrate. The degradation reduced the molar mass of the polymer chains, which acquired greater mobility to approach the equilibrium situation, therefore increasing the value of the enthalpy related to structural relaxation [81]. The cold crystallisation was displaced towards lower temperatures ( $T_{cc}$ ) and tended to disappear during degradation [62]. Finally, the melting enthalpy ( $h_m$ ) and temperature ( $T_m$ ) diminished as a consequence of the crystalline fraction degradation. This behaviour was also visible in the crystallinity degree ( $X_c$ ) that tended to decrease to lower values. Non-significant differences were found in the different substrates.

At the thermophilic and hyperthermophilic temperatures of 58 and 80 °C a similar thermal behaviour was found. However, the changes were generally more severe for the 80 °C temperature. First, the structural relaxation disappeared during degradation in all the substrates, because both 58 and 80 °C were above the glass transition temperature of the PLA (55-60 °C) [54,82]. The cold crystallisation enthalpy ( $h_{cc}$ ) descended and even disappeared, as found at 25 °C. Given the shortening of the polymer chains throughout the degradation, they have increased mobility and, therefore, the ability to crystallise during burial [73]. Both the crystallisation of PLA during degradation and the highly degraded structure prevented the presence of cold-crystallisation during DSC analyses. In terms of crystallinity degree ( $X_c$ ), it increased in the first stage of burial, due to the generation of new crystalline domains by shorter segments that, together with the effect of temperature and humidity, had greater mobility and crystallised [73]. Moreover, the disintegration of the amorphous fraction would result in a higher proportion of crystalline phase with respect to the total mass and, therefore,  $X_c$  increased. Whilst, crystallinity kept growing until day 60 at the thermophilic temperature of 58 °C, at the hyperthermophilic temperature of 80 °C it reached a maximum after day 15 and then decreased until day 60 due to the severe

O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288

degradation. From that point onwards, the PLA collapsed and disintegrated. This behaviour was slightly more pronounced for the synthetic substrate both at 58 and 80 °C.

For the PHBH, only the melting process in the range from 130 to 160 °C could be clearly observed [83]. As found for the PLA, the consideration of degradation temperatures highly above the glass transition of PHBH made difficult the identification of the glass transition and discussion was focused in the melting event and crystalline degree.

During the degradation at the mesophilic temperature of 25 °C, the changes were almost unperceivable. Both the melting temperature ( $T_m$ ) and enthalpy ( $\Delta h_m$ ) remained constant. In the same way, the differences between the substrates were almost irrelevant. The crystallinity degree ( $X_c$ ) along degradation did not revealed significant changes as a function of time and remained around 30% in all the substrates and temperatures.

At the thermophilic temperature of 58 °C, the melting process turned into a bimodal transition, with the fusion of crystalline populations of dissimilar lamellar thickness [84]. The generation of the crystalline fraction with lower thickness during degradation progressed until day 60. From then onwards, the melting transition was again monomodal with an acute peak at higher temperatures ( $T_m$ ). The role of the substrate was non-perceivable in this case. In terms of crystallinity degree ( $X_c$ ), the increase in the temperature enhanced mobility and promoted crystallisation to some extent, reaching values of 37%.

Finally, at the hyperthermophilic temperature of 80 °C, the melting enthalpy ( $\Delta h_m$ ) increased as a function of time. However, the fusion transition revealed a slightly different behaviour for the different substrates. While in the synthetic substrate, the monomodal transition was slightly displaced towards lower temperatures and turned into a more acute peak as a function of time, in the compost and soil substrates, the bimodal transition gained importance. In this case the peak at lower temperatures broadened due to the generation of crystalline domains with lesser lamellar thickness and the peak at higher temperatures sharpened. This behaviour would suggest a slightly diverse degradation pattern in the different substrates due to the prevalence of lower lamellar thickness crystals degradation or general crystalline structure fragmentation, respectively. However, in general, the crystallinity degree ( $X_c$ ) followed a growing tendency and values around 55% were found after 90 days of degradation in all the substrates.

In general, the consequences of degradation in terms of the crystallinity degree ( $X_c$ ) were more significant as the temperature increased, and slightly more relevant in the synthetic substrate both for the PLA and PHBH. Under these conditions, a higher decrease in the melting temperature and a greater increase in the crystallinity degree was found.

#### 4. Conclusions

Although the analysis of the surface macroscopic and microscopic morphology, the thermo-oxidative stability and the thermal properties revealed changes as a function of time, the evaluation of the molar mass allowed for a precise determination of the degradation. In general, chain scission was perceived in all cases as a function of time.

The effect of temperature was critical, implicitly more important than the effect of the substrate. While for PLA, biodegradation at 58 °C and thermal degradation at 80 °C resulted in similar consequences, for PHBH the hyperthermophilic temperature of 80 °C was the most severe condition.

In terms of the substrate, although its influence on the molar mass reduction was not clearly defined, the burial in synthetic substrate at 80 °C were the most severe conditions both for the PLA and PHBH, as demonstrated the macro and microscopic appearance and the change in the microstructure.

From a technological perspective, it may be highlighted that biodegradation at 58 °C may be the most cost-effective condition due to the lower energy supply required and the valuable contribution of microorganisms. For the PLA plates it resulted in complete assimilation in 90 days in the three substrates. Whereas the PHBH plates were not completely disintegrated in this period, a very advanced reduction in molar mass was perceived at 58 °C, which would result in collapse in a short term. In terms of substrate, although the enriched synthetic substrate seemed to be more aggressive, given the similar degradation advance, all of them could be considered according to their availability.

#### Acknowledgements

The authors would like to thank the support of the Spanish Ministry of Science, Innovation and Universities, for the POLYDECARBOCELL project (ENE2017-86711-C3-1-R) and the Chilean Economic Development Agency (CORFO) for the project 13CEI2-21839.

#### References

- [1] M. Tolinski, Towards a Peaceful Coexistence between Bio-based and Fossil Fuel-based Plastics, in: *Plast. Sustain.*, John Wiley & Sons, Inc., 2011: pp. i–xv. doi:10.1002/9781118217849.fmatter.
- [2] PlasticsEurope, *Plastics - the Facts 2019. An analysis of European plastics production, demand and waste data*, 2019. [https://www.plasticseurope.org/download\\_file/force/3183/632](https://www.plasticseurope.org/download_file/force/3183/632).
- [3] J.D. Badia, O. Gil-Castell, A. Ribes-Greus, Long-term properties and end-of-life of polymers from renewable resources, *Polym. Degrad. Stab.* 137 (2017) 35–57. doi:10.1016/j.polymdegradstab.2017.01.002.
- [4] J.P. Greene, Sustainable Plastic Products, in: *Sustain. Plast.*, John Wiley & Sons, Inc., 2014: pp. 145–186. doi:10.1002/9781118899595.ch7.
- [5] M. Braungart, W. McDonough, A. Bollinger, Cradle-to-cradle design: creating healthy emissions – a strategy for eco-effective product and system design, *J. Clean. Prod.* 15 (2007) 1337–1348. doi:10.1016/j.jclepro.2006.08.003.
- [6] J.D. Badia, O. Gil-Castell, R. Teruel-Juanes, A. Ribes-Greus, Recycling of Polylactide, *Ref. Modul. Mater. Sci. Mater. Eng.* (2019). doi:10.1016/B978-0-12-803581-8.10569-7.



- O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288
- [7] O. Gil-Castell, J.D. Badia, A. Ribes-Greus, Suitability of blends from virgin and reprocessed polylactide: Performance and energy valorization kinetics, *J. Renew. Mater.* 6 (2018) 370–382. doi:10.7569/JRM.2017.634170.
- [8] J.D. Badia, E. Strömberg, T. Kittikorn, M. Ek, S. Karlsson, A. Ribes-Greus, Relevant factors for the eco-design of polylactide/sisal biocomposites to control biodegradation in soil in an end-of-life scenario, *Polym. Degrad. Stab.* 143 (2017) 9–19. doi:10.1016/j.polymdegradstab.2017.06.004.
- [9] C.R. Álvarez-Chávez, S. Edwards, R. Moure-Eraso, K. Geiser, Sustainability of bio-based plastics: General comparative analysis and recommendations for improvement, *J. Clean. Prod.* 23 (2012) 47–56. doi:10.1016/j.jclepro.2011.10.003.
- [10] F. von Burkersroda, L. Schedl, A. Göpferich, A.G. F. von Burkersroda, L. Schedl, Why degradable polymers undergo surface erosion or bulk erosion, *Biomaterials.* 23 (2002) 4221–4231. doi:10.1016/S0142-9612(02)00170-9.
- [11] S. Matsumura, Mechanism of biodegradation, in: R. Smith (Ed.), *Biodegrad. Polym. Ind. Appl.*, Woodhead Publishing Limited, 2005: pp. 357–410. doi:10.1533/9781845690762.3.357.
- [12] Y. Tokiwa, B.P. Calabia, Biodegradability and biodegradation of polyesters, *J. Polym. Environ.* 15 (2007) 259–267. doi:10.1007/s10924-007-0066-3.
- [13] G. Kale, R. Auras, S.P. Singh, R. Narayan, Biodegradability of polylactide bottles in real and simulated composting conditions, *Polym. Test.* 26 (2007) 1049–1061. doi:10.1016/j.polymertesting.2007.07.006.
- [14] V.M. Torres A, Li S M, Roussos S, Poly (lactic acid) degradation in soil or under controlled composting and ambient exposure conditions, *J Appl Polym Sci.* 62 (1996) 2295–2302.
- [15] A. Krzan, S. Hemjinda, S. Miertus, A. Corti, E. Chiellini, Standardization and certification in the area of environmentally degradable plastics, *Polym. Degrad. Stab.* 91 (2006) 2819–2833. doi:10.1016/j.polymdegradstab.2006.04.034.
- [16] J.P. Eubeler, S. Zok, M. Bernhard, T.P. Knepper, Environmental biodegradation of synthetic polymers I. Test methodologies and procedures, *TrAC Trends Anal. Chem.* 28 (2009) 1057–1072. doi:10.1016/j.trac.2009.06.007.
- [17] M. Itävaara, S. Karjomaa, J.-F. Selin, Biodegradation of polylactide in aerobic and anaerobic thermophilic conditions, *Chemosphere.* 46 (2002) 879–885. doi:10.1016/S0045-6535(01)00163-1.
- [18] M.-N. Kim, A.-R. Lee, J.-S. Yoon, I.-J. Chin, Biodegradation of poly(3-hydroxybutyrate), Sky-Green® and Mater-Bi® by fungi isolated from soils, *Eur. Polym. J.* 36 (2000) 1677–1685. doi:10.1016/S0014-3057(99)00219-0.
- [19] S.O. Kulkarni, P.P. Kanekar, J.P. Jog, P.A. Patil, S.S. Nilegaonkar, S.S. Sarnaik, P.R. Kshirsagar, Characterisation of copolymer, poly (hydroxybutyrate-co-hydroxyvalerate) (PHB-co-PHV) produced by *Halomonas campisalis* (MCM B-1027), its biodegradability and potential application., *Bioresour. Technol.* 102 (2011) 6625–8. doi:10.1016/j.biortech.2011.03.054.
- [20] T. Apinya, N. Sombatsompop, B. Prapagdee, Selection of a *Pseudonocardia* sp. RM423 that accelerates the biodegradation of poly(lactic) acid in submerged cultures and in soil microcosms, *Int. Biodeterior. Biodegradation.* 99 (2015) 23–30. doi:10.1016/j.ibiod.2015.01.001.
- [21] C. Chuensangjun, C. Pechyen, S. Sirisansaneeyakul, Degradation Behaviors of Different Blends of Poly(lactic Acid Buried in Soil, *Energy Procedia.* 34 (2013) 73–82. doi:10.1016/j.egypro.2013.06.735.
- [22] R. Pantani, A. Sorrentino, Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions, *Polym. Degrad. Stab.* 98 (2013) 1089–1096. doi:10.1016/j.polymdegradstab.2013.01.005.
- [23] H. Yagi, F. Ninomiya, M. Funabashi, M. Kunioka, Anaerobic biodegradation tests of poly(lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge, *Polym. Degrad. Stab.* 94 (2009) 1397–1404. doi:10.1016/j.polymdegradstab.2009.05.012.
- [24] R.K. Sadi, G.J.M. Fehine, N.R. Demarquette, Photodegradation of poly(3-hydroxybutyrate), *Polym. Degrad. Stab.* 95 (2010) 2318–2327. doi:10.1016/j.polymdegradstab.2010.09.003.
- [25] P. Mousavioun, G.A. George, W.O.S. Doherty, Environmental degradation of lignin/poly(hydroxybutyrate) blends, *Polym. Degrad. Stab.* 97 (2012) 1114–1122. doi:10.1016/j.polymdegradstab.2012.04.004.
- [26] L. Pérez Amaro, H. Chen, A. Barghini, A. Corti, E. Chiellini, High Performance Compostable Biocomposites Based on Bacterial Polyesters Suitable For Injection Molding and Blow Extrusion, *Chem. Biochem. Eng. Q.* 29 (2015) 261–274. doi:10.15255/CABEQ.2014.2259.
- [27] J. Sarasa, J.M. Gracia, C. Javierre, Study of the biodesintegration of a bioplastic material waste., *Bioresour. Technol.* 100 (2009) 3764–8. doi:10.1016/j.biortech.2008.11.049.
- [28] R. Gattin, A. Copinet, C. Bertrand, Y. Couturier, Biodegradation study of a starch and poly(lactic acid) co-extruded material in liquid, composting and inert mineral media, *Int. Biodeterior. Biodegradation.* 50 (2002) 25–31. doi:10.1016/S0964-8305(02)00039-2.
- [29] W. Guo, J. Tao, C. Yang, Q. Zhao, C. Song, S. Wang, The rapid evaluation of material biodegradability using an improved ISO 14852 method with a microbial community, *Polym. Test.* 29 (2010) 832–839. doi:10.1016/j.polymertesting.2010.07.004.
- [30] Y. Zhou, Z. Huang, X. Diao, Y. Weng, Y.-Z. Wang, Characterization of the effect of REC on the compatibility of PHBH and PLA, *Polym. Test.* 42 (2015) 17–25. doi:10.1016/j.polymertesting.2014.12.014.
- [31] O. Cadar, M. Paul, C. Roman, M. Miclean, C. Majdik, Biodegradation behaviour of poly(lactic acid) and (lactic acid-ethylene glycol-malonic or succinic acid) copolymers under controlled composting conditions in a laboratory test system, *Polym. Degrad. Stab.* 97 (2012) 354–357. doi:10.1016/j.polymdegradstab.2011.12.006.

- O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288
- [32] M. Funabashi, F. Ninomiya, M. Kunioka, Biodegradability evaluation of polymers by ISO 14855-2., *Int. J. Mol. Sci.* 10 (2009) 3635–54. doi:10.3390/ijms10083635.
- [33] R. Iovino, R. Zullo, M.A. Rao, L. Cassar, L. Gianfreda, Biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions, *Polym. Degrad. Stab.* 93 (2008) 147–157. doi:10.1016/j.polymdegradstab.2007.10.011.
- [34] H.J. Jeon, M.N. Kim, Biodegradation of poly(l-lactide) (PLA) exposed to UV irradiation by a mesophilic bacterium, *Int. Biodeterior. Biodegradation.* 85 (2013) 289–293. doi:10.1016/j.ibiod.2013.08.013.
- [35] M. Kunioka, F. Ninomiya, M. Funabashi, 2006. Kunioka, M., Ninomiya, F., Funabashi, M., Biodegradation of poly(lactic acid) powders proposed as the reference test materials for the international standard of biodegradation evaluation methods, *Polym. Degrad. Stab.* 91 (2006) 1919–1928. doi:10.1016/j.polymdegradstab.2006.03.003.
- [36] V.T. Phuong, M.-B. Coltelli, P. Cinelli, M. Cifelli, S. Verstichel, A. Lazzeri, Compatibilization and property enhancement of poly(lactic acid)/polycarbonate blends through triacetin-mediated interchange reactions in the melt, *Polymer (Guildf).* 55 (2014) 4498–4513. doi:10.1016/j.polymer.2014.06.070.
- [37] Q. Shi, C. Chen, L. Gao, L. Jiao, H. Xu, W. Guo, Physical and degradation properties of binary or ternary blends composed of poly (lactic acid), thermoplastic starch and GMA grafted POE, *Polym. Degrad. Stab.* 96 (2011) 175–182. doi:10.1016/j.polymdegradstab.2010.10.002.
- [38] T. Kijchavengkul, R. Auras, M. Rubino, M. Ngouajio, R. Thomas Fernandez, Development of an automatic laboratory-scale respirometric system to measure polymer biodegradability, *Polym. Test.* 25 (2006) 1006–1016. doi:10.1016/j.polymertesting.2006.06.008.
- [39] T. Leejarkpai, U. Suwanmanee, Y. Rudeekit, T. Mungcharoen, Biodegradable kinetics of plastics under controlled composting conditions., *Waste Manag.* 31 (2011) 1153–61. doi:10.1016/j.wasman.2010.12.011.
- [40] Y. Lemmouchi, M. Murariu, A.M. Dos Santos, A.J. Amass, E. Schacht, P. Dubois, Plasticization of poly(lactide) with blends of tributyl citrate and low molecular weight poly(d,l-lactide)-b-poly(ethylene glycol) copolymers, *Eur. Polym. J.* 45 (2009) 2839–2848. doi:10.1016/j.eurpolymj.2009.07.006.
- [41] E. Petinakis, X. Liu, L. Yu, C. Way, P. Sangwan, K. Dean, S. Bateman, G. Edward, Biodegradation and thermal decomposition of poly(lactic acid)-based materials reinforced by hydrophilic fillers, *Polym. Degrad. Stab.* 95 (2010) 1704–1707. doi:10.1016/j.polymdegradstab.2010.05.027.
- [42] C. Way, K. Dean, D.Y. Wu, E. Palombo, Biodegradation of sequentially surface treated lignocellulose reinforced polylactic acid composites: Carbon dioxide evolution and morphology, *Polym. Degrad. Stab.* 97 (2012) 430–438. doi:10.1016/j.polymdegradstab.2011.11.013.
- [43] Y.-X. Weng, X.-L. Wang, Y.-Z. Wang, Biodegradation behavior of PHAs with different chemical structures under controlled composting conditions, *Polym. Test.* 30 (2011) 372–380. doi:10.1016/j.polymertesting.2011.02.001.
- [44] Y.-X. Weng, Y. Wang, X.-L. Wang, Y.-Z. Wang, Biodegradation behavior of PHBV films in a pilot-scale composting condition, *Polym. Test.* 29 (2010) 579–587. doi:10.1016/j.polymertesting.2010.04.002.
- [45] M.P. Arrieta, E. Fortunati, F. Dominici, J. López, J.M. Kenny, Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends., *Carbohydr. Polym.* 121 (2015) 265–75. doi:10.1016/j.carbpol.2014.12.056.
- [46] M.P. Arrieta, J. López, E. Rayón, A. Jiménez, Disintegrability under composting conditions of plasticized PLA-PHB blends, *Polym. Degrad. Stab.* 108 (2014) 307–318. doi:10.1016/j.polymdegradstab.2014.01.034.
- [47] N. Bitinis, E. Fortunati, R. Verdejo, J. Bras, J.M. Kenny, L. Torre, M.A. López-Manchado, Poly(lactic acid)/natural rubber/cellulose nanocrystal bionanocomposites. Part II: properties evaluation., *Carbohydr. Polym.* 96 (2013) 621–7. doi:10.1016/j.carbpol.2013.03.091.
- [48] N. Bitinis, E. Fortunati, R. Verdejo, I. Armentano, L. Torre, J.M. Kenny, M.Á. López-Manchado, Thermal and bio-disintegration properties of poly(lactic acid)/natural rubber/organoclay nanocomposites, *Appl. Clay Sci.* 93–94 (2014) 78–84. doi:10.1016/j.clay.2014.02.024.
- [49] E. Fortunati, F. Luzi, D. Puglia, F. Dominici, C. Santulli, J.M. Kenny, L. Torre, Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from *Phormium tenax* leaves, *Eur. Polym. J.* 56 (2014) 77–91. doi:10.1016/j.eurpolymj.2014.03.030.
- [50] E. Fortunati, S. Rinaldi, M. Peltzer, N. Bloise, L. Visai, I. Armentano, A. Jiménez, L. Latterini, J.M. Kenny, Nano-biocomposite films with modified cellulose nanocrystals and synthesized silver nanoparticles., *Carbohydr. Polym.* 101 (2014) 1122–33. doi:10.1016/j.carbpol.2013.10.055.
- [51] M.P. Arrieta, E. Fortunati, F. Dominici, E. Rayón, J. López, J.M. Kenny, PLA-PHB/cellulose based films: Mechanical, barrier and disintegration properties, *Polym. Degrad. Stab.* 107 (2014) 139–149. doi:10.1016/j.polymdegradstab.2014.05.010.
- [52] P. Cinelli, M. Schmid, E. Bugnicourt, J. Wildner, A. Bazzichi, I. Anguillesi, A. Lazzeri, Whey protein layer applied on biodegradable packaging film to improve barrier properties while maintaining biodegradability, *Polym. Degrad. Stab.* 108 (2014) 151–157. doi:10.1016/j.polymdegradstab.2014.07.007.
- [53] M. Ramos, E. Fortunati, M. Peltzer, J.M. Kenny, M.C. Garrigós, Characterization and disintegrability under composting conditions of PLA-based nanocomposite films with thymol and silver nanoparticles, *Polym. Degrad. Stab.* 132 (2016) 2–10. doi:10.1016/j.polymdegradstab.2016.05.015.
- [54] O. Gil-Castell, J.D. Badia, S. Ingles-Mascaros, R. Teruel-Juanes, A. Serra, A. Ribes-Greus, Polylactide-based self-reinforced composites biodegradation: Individual and combined influence of temperature, water and compost, *Polym. Degrad. Stab.* 158 (2018) 40–51. doi:10.1016/j.polymdegradstab.2018.10.017.
- [55] G.E.P. Box, J. Stuart Hunter, W.G. Hunter, *Statistics for Experimenters: Design, Innovation and Discovery,*

- O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288
- 2nd ed., Wiley, 2005.
- [56] J.D. Badía, E. Strömberg, A. Ribes-Greus, S. Karlsson, A statistical design of experiments for optimizing the MALDI-TOF-MS sample preparation of polymers. An application in the assessment of the thermo-mechanical degradation mechanisms of poly(ethylene terephthalate), *Anal. Chim. Acta.* 692 (2011) 85–95. doi:10.1016/j.aca.2011.02.063.
- [57] UNE-EN ISO 20200:2015 Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test, 2015.
- [58] UNE-EN ISO 14855-2:2019 Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide - Part 2: Gravimetric measurement of carbon dioxide evolved in a labo, (2019).
- [59] UNE-EN ISO 17556:2013 Plastics - Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved, (2013).
- [60] W.G. Fischer E. W., Sterzel H. J., E.W. Fischer, H.J. Sterzel, G. Wegner, Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions, *Colloid Polym. Sci.* 251 (1973) 980–990. doi:10.1007/BF01498927.
- [61] P.J. Barham, A. Keller, E.L. Otun, P.A. Holmes, Crystallization and morphology of a bacterial thermoplastic: poly-3-hydroxybutyrate, *J. Mater. Sci.* 19 (1984) 2781–2794. doi:10.1007/BF01026954.
- [62] L. Santonja-Blasco, A. Ribes-Greus, R.G. Alamo, Comparative thermal, biological and photodegradation kinetics of polylactide and effect on crystallization rates, *Polym. Degrad. Stab.* 98 (2013) 771–784. doi:10.1016/j.polymdegradstab.2012.12.012.
- [63] M.J. Bajpai PK, Singh I, Comparative studies of mechanical and morphological properties of poly (lactic acid) and polypropylene based natural fiber composites, *J Reinf Plast Compos.* 31 (2012) 1712–24.
- [64] J.D. Badia, L. Santonja-Blasco, A. Martí-nez-Felipe, A. Ribes-Greus, A. Martínez-Felipe, A. Ribes-Greus, Reprocessed polylactide: studies of thermo-oxidative decomposition., *Bioresour. Technol.* 114 (2012) 622–8. doi:10.1016/j.biortech.2012.02.128.
- [65] S.J. Sim, K.D. Snell, S.A. Hogan, J.A. Stubbe, C. Rha, A.J. Sinskey, PHA synthase activity controls the molecular weight and polydispersity of polyhydroxybutyrate in vivo, *Nat. Biotechnol.* 15 (1997) 63–67. doi:10.1038/nbt0197-63.
- [66] A. Giubilini, C. Sciancalepore, M. Messori, F. Bondioli, New biocomposite obtained using poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and microfibrillated cellulose, *J. Appl. Polym. Sci.* (2020) 48953. doi:10.1002/app.48953.
- [67] Q. Qin, W. Takarada, T. Kikutani, Fiber Structure Development of PHBH through Stress-Induced Crystallization in High-Speed Melt Spinning Process, *J. Fiber Sci. Technol.* 73 (2017) 49–60. doi:10.2115/fiberst.2017-0007.
- [68] J. Tuominen, J., Kylma, J., Kapanen, A., Venelampi, O., Itavaara, M., Seppala, Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact, *Biomacromolecules.* 3 (2002) 445–455.
- [69] O. Gil-Castell, J.D. Badia, J. Bou, A. Ribes-Greus, Performance of polyester-based electrospun scaffolds under in vitro hydrolytic conditions: From short-term to long-term applications, *Nanomaterials.* 9 (2019) 786. doi:10.3390/nano9050786.
- [70] O. Gil-Castell, J.D. Badia, I. Ontoria-Oviedo, D. Castellano, B. Marco, A. Rabal, J.J. Bou, A. Serra, L. Monreal, M. Blanes, P. Sepúlveda, A. Ribes-Greus, In vitro validation of biomedical polyester-based scaffolds: Poly(lactide-co-glycolide) as model-case, *Polym. Test.* 66 (2018) 256–267. doi:10.1016/j.polymertesting.2018.01.027.
- [71] A.-F.F. Mohd-Adnan, H. Nishida, Y. Shirai, Evaluation of kinetics parameters for poly(l-lactic acid) hydrolysis under high-pressure steam, *Polym. Degrad. Stab.* 93 (2008) 1053–1058. doi:10.1016/j.polymdegradstab.2008.03.022.
- [72] P.C.G. Shah S.S., Zhu K.J., Poly-DL-lactic acid: Polyethylene glycol block copolymers. The influence of polyethylene glycol on the degradation of poly-DL-lactic acid, (2012).
- [73] J.D. Badia, L. Santonja-Blasco, A. Martínez-Felipe, A. Ribes-Greus, Hygrothermal ageing of reprocessed polylactide, *Polym. Degrad. Stab.* 97 (2012) 1881–1890. doi:10.1016/j.polymdegradstab.2012.06.001.
- [74] J.D. Badia, E. Strömberg, A. Ribes-Greus, S. Karlsson, Assessing the MALDI-TOF MS sample preparation procedure to analyze the influence of thermo-oxidative ageing and thermo-mechanical degradation on poly(Lactide), *Eur. Polym. J.* 47 (2011) 1416–1428. doi:10.1016/j.eurpolymj.2011.05.001.
- [75] J.D. Badia, E. Strömberg, S. Karlsson, A. Ribes-Greus, Material valorisation of amorphous polylactide. Influence of thermo-mechanical degradation on the morphology, segmental dynamics, thermal and mechanical performance, *Polym. Degrad. Stab.* 97 (2012) 670–678. doi:10.1016/j.polymdegradstab.2011.12.019.
- [76] L.M. Araque, T.S. Alves, R. Barbosa, Biodegradation of polyhydroxybutyrate and hollow glass microspheres composite films, *J. Appl. Polym. Sci.* 136 (2019) 47195. doi:10.1002/app.47195.
- [77] O. Gil-Castell, J.D. Badia, T. Kittikorn, E. Strömberg, A. Martínez-Felipe, M. Ek, S. Karlsson, A. Ribes-Greus, Hydrothermal ageing of polylactide/sisal biocomposites. Studies of water absorption behaviour and Physico-Chemical performance, *Polym. Degrad. Stab.* 108 (2014) 212–222. doi:10.1016/j.polymdegradstab.2014.06.010.
- [78] J.D. Badia, L. Santonja-Blasco, R. Moriana, A. Ribes-Greus, Thermal analysis applied to the characterization of degradation in soil of polylactide: II. On the thermal stability and thermal decomposition kinetics, *Polym. Degrad. Stab.* 95 (2010) 2192–2199. doi:10.1016/j.polymdegradstab.2010.06.002.
- [79] J.D. Badia, E. Strömberg, S. Karlsson, A. Ribes-Greus, The role of crystalline, mobile amorphous and rigid

- O. Gil-Castell, R. Andres-Puche, E. Dominguez, E. Verdejo, L. Monreal, A. Ribes-Greus. Influence of substrate and temperature on the biodegradation of polyester-based materials: polylactide and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) as model cases. *Polymer Degradation and Stability* 2020:180;109288
- amorphous fractions in the performance of recycled poly (ethylene terephthalate) (PET), *Polym. Degrad. Stab.* 97 (2012) 98–107. doi:10.1016/j.polymdegradstab.2011.10.008.
- [80] J.D. Badia, F. Vilaplana, S. Karlsson, A. Ribes-Greus, Thermal analysis as a quality tool for assessing the influence of thermo-mechanical degradation on recycled poly(ethylene terephthalate), *Polym. Test.* 28 (2009) 169–175. doi:10.1016/j.polymertesting.2008.11.010.
- [81] E. Rudnik, D. Briassoulis, Comparative Biodegradation in Soil Behaviour of two Biodegradable Polymers Based on Renewable Resources, *J. Polym. Environ.* 19 (2011) 18–39. doi:10.1007/s10924-010-0243-7.
- [82] M. Agarwal, K.W. Koelling, J.J. Chalmers, Characterization of the Degradation of Polylactic Acid Polymer in a Solid Substrate Environment, *Biotechnol. Prog.* 14 (1998) 517–526. doi:10.1021/bp980015p.
- [83] M.C.S. Corrêa, M.L. Rezende, D.S. Rosa, J.A.M. Agnelli, P.A.P. Nascente, Surface composition and morphology of poly(3-hydroxybutyrate) exposed to biodegradation, *Polym. Test.* 27 (2008) 447–452. doi:10.1016/j.polymertesting.2008.01.007.
- [84] B.S. Hsiao, *Polymer Crystallization: The Development of Crystalline Order in Thermoplastic Polymers*, American Chemical Society (ACS), New York, 2001. doi:10.1021/ja015359h.

## ANNEX. OPEN ACCESS POLICIES

The screenshot displays the Sherpa Romeo interface for the journal 'Polymer Degradation and Stability'. It includes a navigation bar with 'About', 'Search', 'Statistics', 'Help', 'Support Us', 'Contact', and 'Admin'. The main content area is titled 'Polymer Degradation and Stability' and is divided into two sections: 'Publication Information' and 'Publisher Policy'.

**Publication Information**

Title	Polymer Degradation and Stability (English)
ISSNs	Print: 0141-3910
URL	<a href="http://www.elsevier.com/wps/product.cws_home/405941/description">http://www.elsevier.com/wps/product.cws_home/405941/description</a>
Publishers	Elsevier [Commercial Publisher]

**Publisher Policy**

Open Access pathways permitted by this journals policy are listed below by article version. Click on a pathway for a more detailed view.

Version	Pathway	Open Access Pathways
Published Version (pathway a)	None, CC BY-NC-ND	PMC, Non-Commercial Repository, Research for Development Repository, +2
Published Version (pathway b)	None, CC BY	Institutional Repository, Subject Repository, PMC, Research for Development Repository, +2
Published Version (pathway c)	None, CC BY, PMC	Institutional Repository, Subject Repository, PMC, Research for Development Repository, +2
Accepted Version (pathway a)	None, CC BY-NC-ND	Author's Homepage
Accepted Version (pathway b)	24m, CC BY-NC-ND	Institutional Repository, Subject Repository
Accepted Version (pathway c)	18m, CC BY-NC-ND	Institutional Repository, Subject Repository
Submitted Version	None	Any Website, +2