

Three-dimensional printing of PLA and PLA/PHA dumbbell-shaped specimens of crisscross and transverse patterns as promising materials in emerging application areas: Prediction study

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ABSTRACT: This paper presents *ex-ante* examination of advanced polymer materials to detect defects and define and minimize the potential failure of novel polymer products before they arise. The effect of build directions on the properties of dumbbell-shaped specimens obtained by three-dimensional printing from polylactide and polylactide/polyhydroxyalkanoate commercial filaments was investigated, as well as the hydrolytic degradation of these specimens at 50 °C and 70 °C. Taking into account previous studies, we have found further dependences of the properties of 3D printed species before and during abiotic degradation from the orientation of printing. The initial assumption that only the contact time with the 3D printer platform leads to an increase in the crystalline phase during printing turned out to be insufficient. Further investigations of individual parts

of the dumbbell-shaped specimens showed that the size of the specimens' surface in contact with the platform also affected the structural ordering of the material.

Keywords: three-dimensional printing, layer orientation, degradation, (bio)degradable polyester, polylactide blend, forensic science, lifetime

1. Introduction

Plastics have become ubiquitous because they have excellent and tailor-made properties with controllable flexibility, ability to be moulded into any shape, are cheap, durable, relatively impermeable, sterilisable, and with a high strength to mass ratio. However, there is growing interest in the application and optimization of biodegradable polymers as an alternative to traditional one. This is caused by growing concerns about land, water and, in particular, marine pollution, which result from the use of nondegradable polymers. Determining the safe life of polymeric materials and understanding the physical and chemical changes in their structure is important for their numerous applications, such as engineering, medical and consumer-good. Continuous development of new materials that are stronger, lighter or more versatile than the previous one must simultaneously lead to an improvement in the safety and environmental issues, because the complexity of recovering value from products increases after their time-of-use. The current challenges associated with the design of products, lead to the development of materials that are stable in use and at the same time, susceptible to microbial attack during organic recycling. Thus, the main objective of current research on (bio)degradable polymeric materials is to determine the course of degradation during virtual tests. For each application of polymeric materials, understanding which of them are optimal for their purposes allows accurate prediction of behaviour and performance over their lifecycle in real conditions. If all factors are well-

considered early enough in the process of developing new materials, potential problems can be avoided. [1-3]

Three-dimensional (3D) printing with various processes as fused deposition modelling (FDM), stereolithography apparatus (SLA), continuous liquid interface production (CLIP), digital light processing (DLP) and selective laser sintering (SLS) is used to create products of unique architecture. Fused deposition modelling, also known as fused filament fabrication is a relatively simple method of 3D objects producing with relatively high resolution and low cost. However, this process requires polymeric filaments with specific physicochemical properties, especially thermal and rheological one, to allow easy processing towards products that meet high performance requirements. [4] According to the McKinsey Global Institute the global market potential for 3D printing will grow to reach 230-550 billion USD in 2025 [5]. The rapid development of materials and technologies used for additive manufacturing is an excellent opportunity to expand (bio)degradable “inks” for the production of personalised materials for everyday use. Polyesters such as polylactide (PLA), polycaprolactone (PCL) and polyhydroxyalkanoates (PHA)s are the most extensively studied classes of (bio)degradable thermoplastic polymers also suitable for additive manufacturing technologies. [6-14]

The widely used thermoplastic PLA seems to be the best candidate for FDM technology because it meets the essential requirements: it is cheap, nontoxic, biocompatible, (bio)degradable, compostable, easily-processed, and its monomer is derived from renewable raw materials, so it can be considered an environmentally-friendly polymer. Moreover, PLA is transparent, easy to colour and quite stiff. However, the lower melting temperature of PLA makes it unsuitable for certain applications. To extend the range of applications of

(bio)degradable polymeric materials containing polylactide, various methods are used to modify PLA depending on intended use [15]. Properties of the PLA can be chemically modified by synthesis of copolymers of lactic acid with lactones or other monomers [16,17], as well as through physical modification, which involves mixing of nonbiodegradable and/or biodegradable synthetic or renewable polymers and/or fillers (e.g. wood or brick) to obtain blends or composites [18-22]. Special additives, such as plasticizers, can effectively modify some properties of polymers, for example mechanical properties [23]. Also the thickness and form of the material can influence on the biodegradation process under soil burial and home composting conditions [24]. Filaments based on bacterial PHA exhibit better mechanical and processing properties, biocompatibility, nontoxicity and rapid (bio)degradation from pure PLA. Therefore, the use of PHAs for 3D printing can open a new field in this area of technology. Processing can affect the mechanical and thermal properties, especially for biodegradable polymers. Extrusion often causes a reduction in viscosity and a decrease in the average molar mass, which worsens the mechanical properties. Mixing time, temperature and drying also influence the degradation of PLA-based materials. [25,26] That is why it is so important to determine the effect of processing conditions on polymer properties and course of hydrolytic degradation.

The aim of the studies was to find further dependences on the processing conditions, 3D printing in horizontal and vertical processing build directions, based on the molar mass and molar-mass dispersity, chemical structure, thermal and mechanical properties analysis of PLA and PLA/PHA dumbbell-shaped specimens. Moreover study of the hydrolytic degradation of PLA and PLA/PHA dumbbell-shaped specimens at 50 °C and 70 °C was performed to assess the influence of incubation temperature on the hydrolytic degradation

behaviour by means of monitoring the changes in mechanical and thermal properties, molar mass and molar-mass dispersity, chemical structure, water absorption and pH of the solution.

2. Materials and methods

2.1. Materials

The materials used in this study were two commercial 3D printing filaments: PLA filament (Orbi-Tech, Germany) and PLA/PHA blend filament (ColorFabb, The Netherlands). Material characteristic, including the determination of PHA component of the PLA/PHA blend was described in [27].

2.2. Fabrication of 3D-printed dumbbell-shaped specimens

PLA and PLA/PHA dumbbell-shaped specimens type 1BA (ISO 527 standard [28]) were obtained using fused deposition modelling printer (FLASHFORGE Dreamer dual extrusion 3D printer). Material preparation and characteristic were described in [27], (Fig. 1).

Fig. 1. Two different processing build directions used to obtain the dumbbell-shaped specimens by 3D fused deposition modelling printer; H – parallel direction (horizontal) and V – perpendicular direction (vertical).

2.3. Hydrolytic degradation under laboratory condition

For the degradation experiments the dumbbell-shaped specimens were incubated at 50 °C and 70 °C (± 0.5) over a period of 70 days. Degradation experiment was described by [27].

The dried films were weighed on an analytical electronic balance (Radwag WAS 160/X,

repeatability 0.1 mg) to calculate the mass changes according to [25]. The molar mass loss was calculated according to [29].

2.4. Water absorption

The mass percentage of water absorbed by the bulk specimen (the degree of moisture absorption) relative to its dry mass was calculated according to the following equation:

$$WA = [(m_0 - m_1)/m_1] \times 100;$$

where WA – water absorption of the specimen [%], m_0 – total mass of the specimen after staying in water medium [g], m_1 – mass of dry matter of a specimen [g].

2.5. Methods

2.5.1. Gel permeation chromatography (GPC) analysis

The molar mass and molar-mass dispersity of the filaments and dumbbell-shaped specimens were determined using gel permeation chromatography conducted in chloroform solution at 35 °C with an eluent flow rate of 1 mL/min using a Viscotek VE 1122 (Malvern, Worcestershire, UK) pump with two Mixed C PLgel styragel columns (Agilent, Santa Clara, CA, USA) in series and a Shodex SE 61 RI detector (Showa Denko, Munich, Germany). Polystyrene standards (Calibration Kit S-M-10, Polymer Laboratories) with narrow molar-mass dispersity were used to generate a universal calibration curve. The samples were measured using OmniSEC 5.0 (Viscotek) software.

2.5.2. Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were recorded using a Thermo Scientific model Nicolet 6700 at room temperature in attenuated total reflection (ATR) mode with a diamond crystal. Sixty-four scans were collected in the range of 500-4000 cm^{-1} wave numbers with a spectral resolution

of 4 cm^{-1} . A background scan of a clean diamond crystal was acquired before scanning the samples.

2.5.3. Scanning electron microscope (SEM)

SEM studies were performed using of a Quanta 250 FEG (FEI Company, USA) high resolution environmental scanning electron microscope operated at 5 kV acceleration voltages. The samples were observed without coating under low vacuum (80 Pa) using a secondary electron detector (Large Field detector).

2.5.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed using a DMA 2980 TA Instruments analyser. Measurements were made using a film tension clamp for the bars prepared from middle part of dumbbell-shaped specimens with thicknesses of 1.7-2 mm, widths of 4-5 mm and lengths of 8-9 mm. The samples were oscillated at a single frequency of 1 Hz with an oscillation amplitude of 5 μm . Using the tension clamp, a 0.01 N static force and 120 % autostrain were applied to the sample. Mechanical spectra were obtained using the temperature trace rate of 3 $^{\circ}\text{C}/\text{min}$, starting from $-80 \text{ }^{\circ}\text{C}$ and ending just above the glass transition temperature (T_g) of the samples. The changes in the storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) were recorded as a function of temperature. The glass transition temperature of the tested samples was taken as the temperature of the loss factor peak (T_{tan}) at which the maximum of the $\tan \delta$ peak was exhibited.

2.5.5. Differential scanning calorimetry (DSC)

Thermal characteristics of the materials were obtained using the TA-DSC Q2000 apparatus (TA Instruments, Newcastle, DE, USA). The instrument was calibrated with high purity indium. The first heating run of the initial sample in which the thermal history is suppressed

and the second heating run of the sample after rapid cooling were acquired from $-30\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$ at the heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$. All of the experiments were performed under a nitrogen atmosphere with the nitrogen flow rate of $50\text{ mL}/\text{min}$, using aluminum sample pans. The melting temperature (T_m) was taken as the peak temperature maximum of that melting endotherm, and the glass transition temperature was taken as the midpoint of the heat capacity change of the amorphous sample obtained by quenching the melted samples from melt ($220\text{ }^{\circ}\text{C}$).

2.5.6. Mechanical properties

The mechanical properties of the samples were determined by conducting tensile tests, which were carried out in accordance with norm ISO 527 in an Instron 4204 universal testing machine (England) equipped with a 1 kN cell load. The crosshead speed was $20\text{ mm}/\text{min}$. The system controls and data analysis were performed using the supplied Instron IX.

2.5.7. pH analysis

The pH measurements of the degradation solutions were at $T = 23.0 \pm 2.0\text{ }^{\circ}\text{C}$ using a Mettler Toledo SevenMulti S40 pH-meter (resolution: $\pm 0.1\text{ mV}$, $\pm 0.001\text{ pH}$ units) equipped with a InLab Science Pro 3-in-1 electrode with reference system ARGENTHALTM and a Ag^+ trap and $3\text{ mol}/\text{L}$ KCl reference inner electrolyte (Metrohm, Switzerland). Calibration of the electrode was performed using buffers (Mettler Toledo, Switzerland) of $\text{pH } 4.01 \pm 0.02$, $\text{pH } 7.00$ and $\text{pH } 9.21 \pm 0.02$ at $T = 23.0 \pm 2.0\text{ }^{\circ}\text{C}$.

3. Results and discussion

3.1. Properties of 3D-printed dumbbell-shaped specimens

Previous studies have shown that the processing conditions, in particular the sample contact time with the printer platform and filament arrangement according to the printing algorithm, leads to different thermal and mechanical properties of material before and during degradation of PLA and PLA/PHA specimens. [27] To more accurately examine the effect of build directions on the properties of 3D-printed dumbbell-shaped specimens obtained from PLA and PLA/PHA commercial filaments were also investigated using GPC, FTIR and DMA techniques.

The changes of the dumbbell-shaped specimens' molar mass and molar-mass dispersity after 3D printing in horizontal and vertical directions were evaluated by GPC experiment. The results indicate that PLA and PLA/PHA filament did not result in a significant degradation revealed as a molar mass reduction or a broadening of molar-mass dispersity (data not shown) during 3D printing in both processing build directions. In contrast, structural analysis of the filaments and dumbbell-shaped specimens obtained by 3D printing and examined by means FTIR analysis showed some differences (Fig. 2).

Fig. 2. Overlay of selected FTIR spectra of PLA and PLA/PHA filaments and dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions.

All spectra showed the main bands which belong to functional group of PLA. Due to the low PHA content in the PLA/PHA blend, it is difficult to distinguish bands which belong to functional groups of PHA, therefore, there were no significant differences between spectra of the PLA and PLA/PHA blend specimens. A slight shift towards higher wavenumbers of the carbonyl group stretching vibration (at 1746 cm^{-1} in the filament) indicated an increase

in crystalline phase during 3D printing in both processing build directions with respect to the filament (see extended region in Fig. 2). This increase is more pronounced in horizontal build directions and also is more pronounced in PLA/PHA dumbbell-shaped specimen which was confirmed also by DSC analysis (see Fig. 4) [27].

The viscoelastic properties of PLA and PLA/PHA dumbbell-shaped specimens obtained using the DMA method are presented in Fig. 3 where the storage modulus and loss modulus versus the temperature at a frequency of 1 Hz for the specimens printed in horizontal and vertical directions are plotted.

Fig. 3. Storage modulus and loss modulus curves as a function of temperature for dumbbell-shaped specimens: 1 (green line) – PLA printed in horizontal, 2 (black line) – PLA printed in vertical, 3 (red line) – PLA/PHA printed in horizontal and 4 (blue line) – PLA/PHA printed in vertical directions.

3D printing for PLA in horizontal and vertical processing build directions seems to not affect its storage modulus changes both in glassy and rubbery-like states. The situation is changed for PLA/PHA blend, for which could be observed a clear difference of storage modulus values in whole measurement range, although the trend of E' changes in the function of temperature is identical for samples obtained both in horizontal and vertical processing build directions. The PLA/PHA blends gives two peaks in the loss modulus curves corresponded to glass transition of two individual components of this system. The addition of PHA significantly decreased maximum value of temperature dependence of loss modulus both for horizontal and vertical processing build directions. The detailed dynamic

mechanical properties of the PLA and PLA/PHA specimens obtained by 3D printing in horizontal and vertical processing build directions are given in Table 1.

Table 1. The viscoelastic parameters of the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) processing build directions.

	PLA-H	PLA-V	PLA/PHA-H	PLA/PHA-V
E' [MPa]	4264	4267	4198	3469
$T_{E''}$ [°C]	68.3	66.7	10.5/64.4	15.6/72.7
E'' [MPa]	693	734	397	367
T_{tan} [°C]	74.8	73.9	10.4/71.6	15.9/77.7
$\tan \delta$	2.594	2.690	1.953	2.332

E' – storage modulus at room temperature, $T_{E''}$ – temperature of the loss modulus peak, E'' – loss modulus at maximum, T_{tan} – temperature of the loss factor peak taken as T_g , $\tan \delta$ – loss factor at maximum

In order to evaluate the changes in the thermal properties of the tested samples as a consequence of the thermal history during the processing by 3D printing, DSC analysis was conducted (Fig. 4). The cold crystallization temperature (T_{cc}), the melting temperatures and the enthalpy values (ΔH_{cc} and ΔH_m) were measured from the first calorimetric trace (first heating run) for the plain sample.

Fig. 4. DSC curves (first heating run at 20 °C/min) for the dumbbell sides and central section of PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions.

The central section of the PLA/PHA dumbbell-shaped specimens obtained by 3D printing in the horizontal direction has the same temperature as in platform on whole underside layer surface (accumulates more heat since it has a smaller surface area) and therefore the rate of crystallization in this place is the greatest contrary to specimens obtained by 3D printing in vertical direction. The central section of the dumbbell-shaped specimens obtained by 3D printing in vertical direction is the farthest from the platform and therefore the lowest rate of crystallization is observed due to lower temperature than in platform. Because of the temperature gradient the degree of crystallization should be different in different specimen section; highest in underside layer and lowest in the middle and at the other end of specimen.

3.2. The effect of build directions on the hydrolytic degradation of PLA and PLA/PHA dumbbell-shaped specimens

The hydrolytic degradation of PLA and PLA/PHA dumbbell-shaped specimens at 50 °C and 70 °C was performed under the laboratory conditions over a period of 70 days. The effect of build directions on the degradation of 3D-printed dumbbell-shaped specimens was more visible for degradation at 50 °C, therefore this degradation requires a deeper analysis. The progress of material hydrolysis was estimated by material examination and failure analysis (macroscopic observations of the specimens' surfaces), specimens mass loss, molar mass, mechanical and thermal properties changes and water absorption of the specimens as well as pH of the degradation medium during the performed experiments.

Macroscopic evaluation of the dumbbell-shaped specimens after 70 days of degradation process at 50 °C showed erosion in the form of the crack of the specimens printed in horizontal processing build direction and disintegration of the specimens with vertical processing build direction (Fig. 5). It is interesting that for vertically printed samples, disintegration occurs much faster. Weaker cohesion between two adjacent printed layers caused this effect.

Fig. 5. Macrographic images of the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before (A) and after 70 days of hydrolytic degradation test at and 50 °C (B), where significant differences in the degree of degradation between specimens were observed.

The degradation process in demineralised water resulted in a decrease in mass (Fig. 6) of the specimens from the beginning of the experiment for both ageing temperatures (50 °C and 70 °C). The progress of degradation greatly increased at temperatures above the glass transition of PLA, therefore, the degradation progress at 50 °C was slower [20–31].

Fig. 6. Mass loss of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions as a function of incubation time during the degradation process at 50 °C and 70 °C.

There are no significant differences in mass loss between specimens degraded at 70 °C, however, the specimens printed in vertical direction showed higher values of mass loss as a

result of weaker cohesion between layers and faster disintegration of the specimens. It should be noted that only the PLA specimen printed in horizontal direction degraded at 50 °C showed mass loss 50 % lower than other samples degraded at this temperature. This sample also has the smallest loss in molar mass (PLA-H, Fig. 7). It seems that probably a larger degree of structural order of specimens obtained by 3D printing in horizontal direction reduces the degradation. It is known that the degradation progress depends on the phase morphology and faster water uptake in amorphous phase.

Fig. 7. Overlay of selected GPC chromatograms of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (0) and at the equal molar mass loss after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C.

During the first stage, 70 days of degradation at 50 °C and 7 days of degradation at 70 °C, the molar mass of PLA dumbbell-shaped specimens decreased more than 93 % (98 % for both PLA specimens degraded at 70 °C, 97 % and 93 % for dumbbell-shaped specimens printed in vertical and horizontal directions, respectively and degraded at 50 °C) with a slight mass loss. The same trends show PLA/PHA dumbbell-shaped specimens (Figs. 6 and 7), which is typical for the hydrolytic degradation mechanism. The degradation of polyesters, especially of PLA, in an aqueous environment occurs through the hydrolysis of ester bonds autocatalysed by carboxy terminal groups, and the hydrolysis rate increases with degradation time. The molar-mass dispersity increases in the first stage, with a maximum together with molar mass loss of more than 90 %. Then the molar-mass loss

slowed down and low-molar-mass compounds begin to be removed from the polymer matrix with a significant pH decrease of degradation medium (data not shown). The catalytic effect of the carboxy terminal groups is reduced and the molar mass loss slowed down with increase of mass loss. [25,32] The results showed decrease in mass loss in the first stage at both temperatures towards PLA specimens. It is known that in the first stage, the addition of PHA in particular poly(3-hydroxybutyrate) (PHB) reduces the rate of degradation because of its more hydrophobic character as well as the increased crystallinity of the PLA/PHA blends, since the degradation progress depends on the phase morphology and faster water uptake in amorphous phase. [8,19,33,34] Also, hollow spaces in the polymer matrix caused by arrangement of the filament (crisscross pattern) promote water penetration and water absorption (Fig. 8) and therefore degradation.

Fig. 8. Water absorption of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions as a function of incubation time during 7 days of the degradation process (when there is no significant specimens mass loss) at 50 °C and 70 °C.

PLA is more hydrophilic and should absorb more water than blend of PLA with PHA, which is more hydrophobic, however, the phase separation of the immiscible blend leading to pit domains made the differences imperceptible. [34] In this case, the build direction is more important. Specimens printed in the horizontal direction absorbed more water than those printed in vertical direction, both for the PLA and for the PLA/PHA in order: horizontal printed specimens degraded at 70 °C > vertical printed specimens degraded at 70

°C>horizontal printed specimens degraded at 50 °C>vertical printed specimens degraded at 50 °C, respectively. This phenomenon is associated with orientation and defects of the filament layers. The polymer matrix had defects (caused by arrangement of the filament) as hollow spaces, air gaps formed during 3D printing in the horizontal direction, which to some extent increased the absorption of the material despite the fact that the specimen was thinner by 13 %. Interestingly, the PLA specimen printed in horizontal direction and degraded at 50 °C behaves differently. It absorbed as much water as PLA/PHA specimen under the same conditions, but the degradation progress is less significant. The absorption of water is not necessarily chemical in nature and does not have to be associated with higher hydrolytic degradation. Water can penetrate pores and holes between crystals through physical interactions. [35]

In order to evaluate the effect of the hydrolytic degradation and failure rate on the mechanical performance of the PLA and PLA/PHA dumbbell-shaped specimens, tensile tests up to failure were conducted. Fig. 9 shows the Young's modulus (E), tensile strength (σ_y), and elongation at break (ϵ_R) of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing as a function of the processing build direction. The specimens after degradation at 50 °C for more than 7 days and at 70 °C for more than 3 days disintegrated, which made analysis impossible.

Fig. 9. Young's modulus, tensile strength, and elongation at break of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (0) and after 3 days of hydrolytic degradation at 50 °C (3/50) and 70 °C (3/70) as well as after 7 days of hydrolytic degradation at 50 °C (7/50).

Transverse orientation only slightly increased the Young's modulus for vertical processing build direction and only for the PLA/PHA blend at the beginning of degradation at 50 °C. A significant decrease was observed for PLA dumbbell-shaped specimen printed in horizontal direction, and also a small for vertical build direction [27,36], along with a tensile strength decrease. The PLA dumbbell-shaped specimens exhibited deformation during degradation. It is known that PLA is deforms at relatively low temperatures, especially above the glass transition temperature. The PHA component of the PLA/PHA dumbbell-shaped specimens led to a significant reduction in deformation as well as increased thermal stability during degradation [27], thus these specimens were also stiffer and stronger (Young's modulus and tensile strength were higher). Young's modulus was lower at the beginning of hydrolytic degradation for PLA specimens since the degradation process softens the polymer as a result of self-compatibilization and the plasticizing effect of the oligomeric products generated during degradation. High levels of strain accelerate stress relaxation, because the progress of degradation increases with strain increases. The material also becomes less viscous during hydrolytic degradation and returns to a relaxed state more quickly. [37-40] In general, the materials become softer but less strong and less flexible, as also the elongation at break decreased for all specimens where the notch effect occurs (except for PLA dumbbell-shaped specimen printed in vertical build direction for which elongation at break increased what corralled with decrease of tensile strength). After a longer period of degradation, especially at 70 °C, the degree of crystallinity and therefore brittleness of the material increases and become stiffer, less strong and less flexible.

Differences in the behaviour of the PLA specimen printed in horizontal direction can be

explained by its greater melting temperature value and higher degree of crystallinity (Fig. 10, Table 2).

Fig. 10. DSC curves (first heating run at 20 °C/min) for the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions after 70 days of hydrolytic degradation at 50 °C.

The glass transition temperature, the cold crystallization temperature, the melting temperature and the enthalpy values were obtained from the first calorimetric trace (first heating run) and for the amorphous samples from the second heating run after rapid cooling from the melt for all specimens after 42 and 70 days of hydrolytic degradation at 50 °C and after 7 and 42 days of hydrolytic degradation at 70 °C. The T_g was calculated to be the temperature at the inflection point of the phenomenon (Tables 1 and 2).

Table 2. Calorimetric parameters before (0) and during hydrolytic degradation (after 7, 42 and 70 days of incubation) of PLA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions. Specimens after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C have over 90 % molar mass loss (20 °C/min).

Sample	PLA-H	PLA-V*	PLA-H	PLA-H	PLA-V	PLA-V	PLA-H	PLA-H	PLA-V	PLA-V
Time [days]	0	0	7	70	7	70	42	42	42	42
Temp. [°C]	-	-	70	50	70	50	50	70	50	70
I-heating run										
T_m [°C]	150.7	150.3	138.5/142.2	140.4	138.3/142.5	133.0	155.8	128.1	153.0	127.5
ΔH_m [J/g]	0.98	1.83	61.12	50.03	59.43	54.70	29.19	49.24	26.72	58.30
T_{cc} [°C]	118.0	122.7	-	-	-	-	105.8	-	98.9	-
ΔH_{cc} [J/g]	-0.93	-1.82	-	-	-	-	-28.93	-	-25.89	-
II-heating run										
T_g [°C]	62.2	61.7	43.5	48.1	43.8	43.7	59.1	43.3	58.2	42.0
Δc_p [J/g°C]	0.50	0.50	0.58	0.52	0.62	0.58	0.57	0.60	0.59	0.54

T_m [°C]	-	-	138.3	140.6	138.0	129.9	-	126.6	150.0	125.8
ΔH_m [J/g]	-	-	22.31	12.32	18.91	13.85	-	3.43	0.22	1.69
T_{cc} [°C]	-	-	112.0	116.1	112.9	110.4	-	110.5	-	110.5
ΔH_{cc} [J/g]	-	-	-22.27	-12.16	-18.68	-13.83	-	-3.22	-	-1.67

T_g – glass transition temperature, Δcp – the increment of heat capacity at the glass transition, T_m – melting temperature, ΔH_m – melting enthalpy, T_{cc} – maximum of the exothermic peak of the cold crystallization temperature, ΔH_{cc} – cold crystallization enthalpy; * – average values from both sides of the dumbbell

Table 3. Calorimetric parameters before (0) and during hydrolytic degradation (after 7, 42 and 70 days of incubation) of PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions. Specimens after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C have over 90 % molar mass loss (20 °C/min).

Sample	PLA/PHA-H	PLA/PHA-V*	PLA/PHA-H	PLA/PHA-H	PLA/PHA-V	PLA/PHA-V	PLA/PHA-H	PLA/PHA-H	PLA/PHA-V	PLA/PHA-V
Time [days]	0	0	7	70	7	70	42	42	42	42
Temp. [°C]	-	-	70	50	70	50	50	70	50	70

I-heating run

T_m [°C]	153.5/172.2	154.0/172.6	142.5/152.7	132.3/148.1	140.4/146.4	137.4/143.3	141.7/153.9	123.2/147.0	153.4/161.0	123.1/147.1
ΔH_m [J/g]	16.16	11.96	60.94	56.5	57.87	55.06	35.60	47.09	35.65	58.22
T_{cc} [°C]	116.5	125.9	-	-	-	-	-	-	-	-
ΔH_{cc} [J/g]	-16.70	-11.79	-	-	-	-	-	-	-	-

II-heating run

T_g [°C]	1.9/62.8	1.9/60.4	37.1	34.7	31.62	35.3	48.4	-9.6/30.5	49.1	31.5
Δc_p [J/g°C]	0.04/0.49	0.04/0.49	0.56	0.58	0.52	0.59	0.52	0.03/0.57	0.53	0.56
T_m [°C]	153.4/172.4	152.8/174.5	131.8/139.2	122.8/127.7	127.6/137.8	124.5/128.9	148.4/152.4	114.6/120.3	150.8/152.6	115.33/120.9
ΔH_m [J/g]	0.24	0.56	44.78	37.97	42.42	36.94	28.81	19.90	24.82	22.39
T_{cc} [°C]	136.8	141.5	96.1	95.7	94.2	95.9	117.1	98.1	122.3	97.7
ΔH_{cc} [J/g]	-0.23	-0.53	-44.09	-37.69	-42.0	-36.80	-28.79	-19.26	-24.11	-22.07

T_g – glass transition temperature, Δc_p – the increment of heat capacity at the glass transition, T_m – melting temperature, ΔH_m – melting enthalpy, T_{cc} – maximum of the exothermic peak of the cold crystallization temperature, ΔH_{cc} – cold crystallization enthalpy; * – average values from both sides of the dumbbell

During hydrolytic degradation on DSC thermograms the first heating run shows a small glass transition relaxation (between 34 °C and 66 °C) followed by melting process (Fig. 10). Only PLA dumbbell-shaped specimens printed in horizontal and vertical directions after 42 days at 50 °C exhibited a cold crystallization effect during the first heating run at 20 °C min⁻¹. During the second heating run at 20 °C min⁻¹, the same specimens were the only ones that did not show a cold crystallization effect. It may be a plasticization/nucleation effect (by degradation products) that reduces T_g and T_m and allows crystallization in the first heating run. However, in the second run after a rapid cooling, the specimens had no chance of nucleation during cooling and therefore only showed T_g . The maximum of the exothermic peak of the cold crystallization temperature decreased as the incubation time increased. Therefore, during the degradation process, the shorter chains could begin to freely crystallize at lower temperatures because of their higher mobilities except for both PLA/PHA dumbbell-shaped specimens degraded at 70 °C. The degradation process increased the values of the cold crystallization enthalpy only during degradation at 50 °C. An increase in the cold crystallization enthalpy indicates an increase in the number of polymer chains that are involved in the crystallization process during degradation together with a decrease in T_g , which allows the crystallization to begin at a lower temperature, thus extending its time.

During the first heating run multiple melting peaks in the DSC curve have been noted for both PLA/PHA dumbbell-shaped specimens after 7 days degradation at 70 °C. This means that at the beginning of degradation two different crystalline distributions are formed, the lower melting temperature peak, corresponding to the population with a lower size lamella, is located at 138 °C (T_{m1}), and the higher temperature peak, corresponding to the crystalline

conformations that have a larger size lamella, appears at 142 °C (T_{m2}). For PLA/PHA dumbbell-shaped specimens printed in vertical direction, at cooling rate of 1 °C/min the two exotherms at 122.6 °C and 97.6 °C were observed. Further heating at 1 °C/min, after previous cooling at 1 °C/min, exhibited the two endotherms corresponding probably to the two crystalline distributions of blend specimen with different molar mass or to the two components of the blend (PLA and PHA). The presence of PHA can not only plasticize [27,41] but can also initiate the crystallization of the blends by induction/nucleation as the nucleation agent (ΔH_{cc} increases significantly, T_g , and T_{cc} decrease significantly, Tables 1 and 2) [27,42]. One glass transition temperature was observed for the PLA/PHA specimens indicating that the PLA/PHA blend becomes miscible during degradation.

After degradation, a higher melting temperature, glass transition temperature and molar mass of the PLA specimen printed in horizontal direction were observed. Generally, polymers with higher T_g will also have higher T_m . The value of T_m depends on the chain stiffness, structural regularity (isotactic, syndiotactic, etc.), molar mass and branching degree of the chain. Slower molar mass loss generated fewer amount of polymer chain ends (carboxy terminal groups), which can be considered as impurities that lower the melting temperature of the polymer crystals to a lesser extent than for the other specimens. It is known that the cleavage of polyester chains is catalysed by carboxy terminal groups, and the rate of this reaction is proportional to the concentrations of water and ester bonds that can be constant during the hydrolysis, due to the presence of a large excess of water molecules and of ester linkages of polymer chains. The degree of crystallinity has large impact on the progress of PLA hydrolysis. The crystalline phase absorbs much less water. The increase in the crystallinity after several days of hydrolytic degradation contributes to

its slowing down, since the diffusion of water is more limited by PLA crystalline phase into the polymer matrix. The polylactide sample too quickly become orderly during hydrolytic degradation, which slowed degradation down. [43]

Microscopic evaluation of the specimen surfaces after 70 days of hydrolytic degradation at 50 °C showed erosion due to water absorption as a crack for PLA specimen printed in vertical direction and PLA/PHA dumbbell-shaped specimen printed in horizontal direction (Fig. 11). The smooth surface of PLA dumbbell-shaped specimen printed in a horizontal direction confirms that this specimen has become softer as revealed by mechanical analysis (Figs. 9 and 11).

Fig. 11. Selected SEM micrographs of upper (U) and underside (B) layers of PLA and PLA/PHA dumbbell-shaped specimens surface obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (A) and after 70 days of hydrolytic degradation test at 50 °C (B).

4. Conclusions

Originally it has been found that the processing conditions, in particular the contact time with the 3D printer platform, lead to an increase in crystalline phase during printing [27]. Both the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal direction were more orderly. The new results of investigation of processing conditions and build directions on the properties of dumbbell-shaped specimens from sustainable polymeric materials, PLA and PLA/PHA filaments showed that not only the contact time with the 3D printer platform, leads to an increase in the crystalline phase

during printing, but also smaller specimens' surface area. The central section of the dumbbell-shaped specimens obtained by 3D printing in horizontal direction accumulates more heat and therefore the rate of crystallization in this place is higher.

During hydrolytic degradation, the weaker cohesion between the two printed layers of vertically printed specimens resulted in a faster disintegration time, and thus mass lost. The build direction proved to be a more important parameter conditioning degradation than the hydrophobicity of the specimens. It was originally observed, that before degradation vertical specimens have improved mechanical properties compared to horizontal printed specimens, and after degradation the material become softer but less strong and less flexible. In general, the three-dimensional printing direction is an important parameter that should be taken into account when designing the application of 3D printed materials.

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Author Contributions

This manuscript was written through contributions of all authors. Joanna Rydz contributed 50 %, Jennifer Gonzalez Ausejo contributed 10 %, while the other authors contributed within 40 % equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

References

- [1] Report. The Royal Society & The Royal Academy of Engineering, Nanoscience and nanotechnologies: opportunities and uncertainties. London: The Royal Society, 2004.
- [2] Hazell J. Getting it right from the start. Developing a circular economy for novel materials. London: Green Alliance, 2017.
- [3] Laycock B, Nikolić M, Colwell JM, Gauthier E, Halley P, Bottle S, George G. Lifetime, prediction of biodegradable polymers. *Prog Polym Sci* 2017;71:144-189. doi:10.1016/j.progpolymsci.2017.02.004.
- [4] Włodarczyk J, Sikorska W, Rydz J, Johnston B, Jiang G, Radecka I, Kowalczyk M. Chapter 6: 3D processing of PHA containing (bio)degradable materials. In: *Current advances in biopolymer processing & characterization*, M. Koller, (ed.), Biomaterials – properties, production and devices series. New York: Nova Science Publishers, 2017. pp. 121-168.
- [5] Gebler M, Schoot-Uiterkamp AJM, Visser C. A global sustainability perspective on 3D printing technologies. *Energy Policy* 2014;74:158-167. doi:10.1016/j.enpol.2014.08.033.
- [6] Ingrao C, Tricase C, Cholewa-Wójcik A, Kawecka A, Rana R, Siracusa V. Polylactic acid trays for fresh-food packaging: A Carbon footprint assessment. *Sci Total Environ* 2015;37:385-398. doi:10.1016/j.scitotenv.2015.08.023.
- [7] Kale G, Auras R, Singh S, Narayan R. Biodegradability of polylactide bottles in real and simulated composting conditions. *Polym Test* 2007;26:1049-1061. doi:10.1016/j.polymertesting.2007.07.006.
- [8] Musioł M, Sikorska W, Adamus G, Janeczek H, Kowalczyk M, Rydz J. (Bio)degradable polymers as a potential material for food packaging: studies on the (bio)degradation process

of PLA/(R,S)-PHB rigid foils under industrial composting conditions. *Eur Food Res Technol* 2016;242(6):815-823. doi:10.1007/s00217-015-2611-y.

[9] Musioł M, Sikorska W, Kowalczyk M, Adamus G. The development of sustainable bioplastics for new applications in packaging industry. *Int J Environ Agric Res* 2016;2(2):117-124.

[10] Stansbury JW, Idacavage MJ. 3D printing with polymers: challenges among expanding options and opportunities. *Dent Mater* 2016;32:54-64. doi:10.1016/j.dental.2015.09.018.

[11] Masood SH. Intelligent rapid prototyping with fused deposition modeling. *Rapid Prototyp J* 1996;2:24-33. doi:10.1108/13552549610109054.

[12] Cooke MN, Fisher JP, Dean D, Rinnac C, Mikos AG. Use of stereolithography to manufacture critical-sized 3D biodegradable scaffolds for bone in growth. *J Biomed Mater Res Part B Appl Biomater* 2003;64B(2):65-69. doi:10.1002/jbm.b.10485.

[13] Tumbleston JR, Shirvanyants D, Ermoshkin N, Januszewicz R., Johnson AR, Kelly D, Chen K, Pinschmidt R, Rolland JP, Ermoshkin A, Samulski ET, DeSimone JM. Continuous liquid interface production of 3D objects. *Science* 2015;347:1349-1352. doi:10.1126/science.aaa2397.

[14] Chia HN, Wu BM. Recent advances in 3D printing of biomaterials. *J Biol Eng* 2015;9(4):2-14. doi:10.1186/s13036-015-0001-4.

[15] Sanyang ML, Sapuan SM. Development of expert system for biobased polymer material selection: food packaging application. *J Food Sci Technol* 2015;52(10):6445-6454. doi:10.1007/s13197-015-1759-6.

- [16] Olsén P, Borke T, Odelius K, Albertsson A-Ch. ϵ -Decalactone: A thermoresilient and toughening comonomer to poly(L-lactide). *Biomacromolecules* 2013;14:2883-2890. doi:10.1021/bm400733e.
- [17] Hakkarainen M. Aliphatic polyesters: Abiotic and biotic degradation and degradation products. *Adv Polym Sci book series – Polymer*, 2002;157:113-138. Berlin Heidelberg: Springer-Verlag. doi:10.1007/3-540-45734-8_4.
- [18] Rasal RM, Janorkar AV, Hirt DE. Poly(lactic acid) modifications. *Prog Polym Sci* 2010;35:338-356. doi:10.1016/j.progpolymsci.2009.12.003.
- [19] Arrieta MP, López J, Hernández A, Rayón E. Ternary PLA-PHB-limonene blends intended for biodegradable food packaging applications. *Eur Polym J* 2014;50:255-270. doi:10.1016/j.eurpolymj.2013.11.009.
- [20] Arrieta MP, López J, Ferrández S, Peltzer MA. Characterization of PLA-limonene blends for food packaging applications. *Polym Test* 2013;32:760-768. doi:10.1016/j.polymertesting.2013.03.016.
- [21] Arrieta MP, López J, Rayón E, A Jiménez. Disintegrability under composting conditions of plasticized PLA-PHB blends. *Polym Degrad Stab* 2014;108:307-318. doi:10.1016/j.polymdegradstab.2014.01.034.
- [22] Zhang M, Thomas NL. Blending polylactic acid with polyhydroxybutyrate: The effect on thermal, mechanical, and biodegradation properties. *Adv Polym Tech* 2011;30(2):67-79. doi:10.1002/adv.20235.
- [23] Qin Y, Wang Y, Wu Y, Zhang Y, Li H, Yuan M. Effect of hexadecyl lactate as plasticizer on the properties of poly(L-lactide) films for food packaging applications. *J Polym Environ* 2015;23:374-382. doi:0.1007/s10924-014-0702-7.

- [24] Rudnik E, Briassoulis D. Degradation behaviour of poly(lactic acid) films and fibres in soil under Mediterranean field conditions and laboratory simulations testing. *Ind Crops Prod* 2011;33(2011):648-658. doi:10.1016/j.indcrop.2010.12.031.
- [25] Sikorska W, Richert J, Rydz J, Musioł M, Adamus G, Janeczek H, Kowalczyk M. Degradability studies of poly(L-lactide) after multi-reprocessing experiments in extruder. *Polym Degrad Stab* 2012;97:1891-1897. doi:10.1016/j.polymdegradstab.2012.03.049.
- [26] Peinado V, Castell P, García L, Fernández Á. Effect of extrusion on the mechanical and rheological properties of a reinforced poly(lactic acid): Reprocessing and recycling of biobased materials. *Materials* 2015;8(10):7106-7117. doi:10.3390/ma8105360.
- [27] Gonzalez Ausejo J, Rydz J, Musioł M, Sikorska W, Sobota M, Włodarczyk K, Adamus G, Janeczek H, Kwiecień I, Hercog A, Johnston B, Khan HR, Kannappan V, Jones KR, Morris MR, Jiang G, Radecka I, Kowalczyk M. A comparative study of three-dimensional printing directions: The degradation and toxicological profile of a PLA/PHA blend, *Polym Degrad Stab* 2018;152:191-207. doi:10.1016/j.polymdegradstab.2018.04.024.
- [28] ISO 527–2:2012 Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics.
- [29] Rydz J, Adamus G, Wolna-Stypka K, Marcinkowski A, Misiurska-Marczak M, Kowalczyk MM. Degradation of polylactide in paraffin and selected protic media. *Polym Degrad Stab* 2013;98:316-324. doi:10.1016/j.polymdegradstab.2012.09.010.
- [30] Andersson SR, Hakkarainen M, Inkinen S, Södergård A, Albertsson A-C. Polylactide stereocomplexation leads to higher hydrolytic stability but more acidic hydrolysis product pattern. *Biomacromolecules* 2010;11:1067-1073. doi:10.1021/bm100029t.

- [31] Li S, McCarthy S. Further investigations on the hydrolytic degradation of poly(DL-lactide). *Biomaterials* 1999;20:35-44. doi:10.1016/S0142-9612(97)00226-3.
- [32] Hakkarainen M, Albertsson A-C, Karlsson S. Weight losses and molecular weight changes correlated with the evolution of hydroxyacids in simulated in vivo degradation of homo-and copolymers of PLA and PGA. *Polym Degrad Stab* 1996;52:283-291. doi:10.1016/0141-3910(96)00009-2.
- [33] Arrieta MP, Fortunati E, Dominici F, Rayón E, López J, Kenny JM. PLA-PHB/cellulose based films: Mechanical, barrier and disintegration properties. *Polym Degrad Stab* 2014;107:139-149. doi:10.1016/j.polymdegradstab.2014.05.010.
- [34] Rydz J, Wolna-Stypka K, Adamus G, Janeczek H, Musioł M, Sobota M, Marcinkowski A, Krzan A, Kowalczyk M. Forensic engineering of advanced polymeric materials. Part 1 – degradation studies of polylactide blends with atactic poly[(R,S)-3-hydroxybutyrate] in paraffin. *Chem Biochem Eng Q* 2015;29(2):247-259. doi:10.15255/CABEQ.2014.2258.
- [35] ASM International, *Characterization and Failure Analysis of Plastics*, Steve Lampman (ed.), ASM International, Materials Park, USA 2003, pp. 314-322.
- [36] Rollett AD, De Graef M. *Microstructure-Properties Lecture 1: What is Microstructure?* Carnegie Mellon University, Pittsburgh, USA 2015, http://pajarito.materials.cmu.edu/rollett/27301/L12-Composites-part_2-9Nov15.pdf.
- [37] Vieira AC, Guedes RM, Tita V. Constitutive modeling of biodegradable polymers: Hydrolytic degradation and time-dependent behaviour. *Int J Solids Struct* 2014;51:1164-1174. doi:10.1016/j.ijsolstr.2013.12.010.

- [38] Muliana A, Rajagopal KR. Modeling the response of nonlinear viscoelastic biodegradable polymeric stents. *Int J Solids Struct* 2012;49(7-8):989-1000. doi:10.1016/j.ijsolstr.2011.12.007.
- [39] Soares JS. Constitutive Modeling for biodegradable polymers for applications in endovascular stents (PhD Dissertation). Mechanical Engineering Texas A&M University, Texas, USA 2008.
- [40] Panyasart K, Chaiyut N, Amornsakchai T, Santawitee O. Effect of surface treatment on the properties of pineapple leaf fibers reinforced polyamide 6 composites. *Energy Procedia* 2014;56:406-413. doi:10.1016/j.egypro.2014.07.173.
- [41] Malinowski R, Żenkiewicz M, Richert S. Niektóre właściwości modyfikowanego polilaktydu. In: Wróbel G. (ed.). *Polimery i kompozyty konstrukcyjne*. Cieszyn, Gliwice: Logos Press, 2011. pp 299-305.
- [42] Di Lorenzo ML, Sajkiewicz P, Gradys A, La Pietra P. Optimization of melting conditions for the analysis of crystallization kinetics of poly(3-hydroxybutyrate). *e-Polymers* 2009;27:1. doi:10.1515/epoly.2009.9.1.313.
- [43] Benali S, Aouadi S, Dechief A-L, Murariu M, Dubois P. Key factors for tuning hydrolytic degradation of polylactide/zinc oxide nanocomposites. *Nanocomposites* 2015;1(1):51-61. doi:10.1179/2055033214Y.0000000007.

Figures captions

Fig. 1. Two different processing build directions used to obtain the dumbbell-shaped specimens by 3D fused deposition modelling printer; H – parallel direction (horizontal) and V – perpendicular direction (vertical).

Fig. 2. Overlay of selected FTIR spectra of PLA and PLA/PHA filaments and dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions.

Fig. 3. Storage modulus and loss modulus curves as a function of temperature for dumbbell-shaped specimens: 1 (green line) – PLA printed in horizontal, 2 (black line) – PLA printed in vertical, 3 (red line) – PLA/PHA printed in horizontal and 4 (blue line) – PLA/PHA printed in vertical directions.

Fig. 4. DSC curves (first heating run at 20 °C/min) for the dumbbell sides and central section of PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions.

Fig. 5. Macrographic images of the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before (A) and after 70 days of hydrolytic degradation test at and 50 °C (B), where significant differences in the degree of degradation between specimens were observed.

Fig. 6. Mass loss of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions as a function of incubation time during the degradation process at 50 °C and 70 °C.

Fig. 7. Overlay of selected GPC chromatograms of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (0) and at the equal molar mass loss after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C.

Fig. 8. Water absorption of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions as a function of incubation time during 7 days of the degradation process (when there is no significant specimens mass loss)

at 50 °C and 70 °C.

Fig. 9. Young's modulus, tensile strength, and elongation at break of PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (0) and after 3 days of hydrolytic degradation at 50 °C (3/50) and 70 °C (3/70) as well as after 7 days of hydrolytic degradation at 50 °C (7/50).

Fig. 10. DSC curves (first heating run at 20 °C/min) for the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions after 70 days of hydrolytic degradation at 50 °C.

Fig. 11. Selected SEM micrographs of upper (U) and underside (B) layers of PLA and PLA/PHA dumbbell-shaped specimens surface obtained by 3D printing in horizontal (H) and vertical (V) directions before degradation (A) and after 70 days of hydrolytic degradation test at 50 °C (B).

Tables captions

Table 1. The viscoelastic parameters of the PLA and PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) processing build directions.

Table 2. Calorimetric parameters before (0) and during hydrolytic degradation (after 7, 42 and 70 days of incubation) of PLA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions. Specimens after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C have over 90 % molar mass loss (20 °C/min)

Table 3. Calorimetric parameters before (0) and during hydrolytic degradation (after 7, 42 and 70 days of incubation) of PLA/PHA dumbbell-shaped specimens obtained by 3D printing in horizontal (H) and vertical (V) directions. Specimens after 70 days of degradation at 50 °C and after 7 days of degradation at 70 °C have over 90 % molar mass

loss (20 °C/min).