Forensic Engineering of Advanced Polymeric Materials. Part VI – Degradation of Polyester-based Materials Obtained by Different Processing Methods – Comparative Studies

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ABSTRACT

Both *ex-ante* investigations as well as *ex-post* studies are needed in the area of advanced polymer materials, particularly (bio) degradable polymers, in order to increase efficiency and to define and minimise the potential failure of novel polymer products before and during specific applications. The after-use properties of such materials are also important and therefore in this study, the degradation of polylactide (PLA) films with different thickness and PLA-based films with poly[(R,S)-3-hydroxybutyrate] ((R,S)-PHB), both obtained by extrusion as well as samples of PLA and its blend with polyhydroxyalkanoate (PHA) obtained by 3D printing with different patterns (printing directions) were investigated. The materials were characterised by optical microscopy, gel permeation chromatography and differential scanning calorimetry analysis. The main aspect of this research is to elaborate on new strategies for the comprehensive characterisation of complex polymer systems obtained by different methods. Comparative studies have allowed conclusions to be drawn from research on various materials under similar conditions.

KEY WORDS

Rigid Film; Filament; Extrusion; Three-Dimensional Printing; Degradation; (Bio)degradable Polyester; PLA; PHA.

INTRODUCTION

The most common methods of plastic processing are extrusion and injection moulding. Extrusion is a plastic forming method in which plastic is melted and formed into a continuous profile, the molten plastic is then pushed through a two-dimensional die opening to produces, for example, polymeric films. Injection moulding is a process were molten plastic is injected into one or more cavities in a three-dimensional (3D) mould. Unlike to the traditional extrusion method, this process can produce 3D shaped species. The extrusion method by which three-dimensional articles can be obtained is known as 3D printing, which is a fast-growing technology of new manufacturing process. Thermoplastic polymers are deposited during 3D printing layer by layer onto a platform. The extruder is made up of the printer head, nozzle and gear pump and all of these components work together to pass filament through

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a heating zone and then into the nozzle. Both extrusion and injection methods require specific conditions and characteristics, melt conditions or adhesion, of the polymers used are considered, otherwise problems such as sticking to the platform of a 3D printer or clogging of the nozzle can occur. [1] The properties of extruded or injection-moulded articles, such as the orientation of the polymer chain and the ratio of crystalline to amorphous phases, will depend on the conditions of the moulding operation as well as any thermal treatments used after forming. Depending on the process used, macro- or microscopic differences in the final products will appear. [2-4]

Polyesters, such as polylactide or a group of polymers produced in nature by numerous microorganisms – polyhydroxyalkanoates, belong to a large class of (bio)degradable polymers. PLA and PHA are also thermoplastics, which are a group of polymers that can be processed by both extrusion and injection methods. [5] PLA is a synthetic polymer from a renewable monomer obtained from natural resources such as starch, sugar or cellulose. Polyhydroxyalkanoates are a family of polyesters consisting of over 150 different monomers. PHAs are obtained from bacterial fermentation of sugar or lipids and they are used by bacteria as a storage material. PLA and poly[(R)-3-hydroxybutyrate] (PHB, one of the PHA family), are both brittle at ambient temperature, but the addition of PHB into PLA improves elongation at break and eliminates its time dependency. Therefore, blending PHB and PLA eliminates the physical aging process and improves processing stability. Thus, from the viewpoint of improving the properties of materials, the blends or composites were used as (bio)degradable packages or as resorbable materials in the medical field (such as sutures, implants or capsules). [6-12] Processing can impact on the mechanical properties of polymers: multiple extrusions cause a decrease in viscosity and a reduction in the mean molar mass, which lowers the tensile strength at break [13]. Plasticised PLA showed a decrease in modulus and stress at break [14], although the multiple extrusions did not significantly affect degradation under abiotic conditions [15-17]. Mixing time, temperature and drying also influence the degradation of PLA-based materials [18].

Products made from (bio)degradable polymers after use are susceptible to organic recycling, which reduces the environmental impact of waste packaging and allows for the rational utilisation of these materials under composting conditions in accordance with new trends in the management of this type of waste. However, to make their use more efficient requires basic research to determine the relationship between the structure of such materials (including the topology of the macromolecules) properties and degradation mechanism. Such studies are necessary especially in view of the fact that

bioassimilation of low molar mass degradation products are required. With detailed evaluation and understanding of the relationships between the structure, properties and behaviour before, during and after practical applications, the forensic engineering of advanced polymeric materials can provide versatile products. Classical forensic engineering is considered to be the investigation of materials, products, structures or components that fail or do not function as intended. Despite this, there are also opinions within the scientific community indicating the need to detect problems before they arise. Due to the wide spectrum of potential applications of (bio)degradable polymers in medicine, in the field of compostable polymer packages (especially of long-shelf life products such as cosmetics or household chemicals) as well as in agrichemical formulations, the forensic engineering of advanced polymeric materials can provide basic knowledge and a valuable service by increasing understanding and helping prevent future problems. Such a novel approach may help to design novel polymeric materials and avoid the failures of existing ones. [19-25]

Traditional polymer materials have an adverse effect on the environment. The environmental regulations of the European Union recommend the expanded use of (bio)degradable and/or biobased polymers with a minimised carbon footprint. From the perspective of sustainable development, (bio)degradable polymers are considered as safe for the environment and they are an interesting alternative to conventional polymers. There is also a growing demand for (bio)degradable polymers that are designed as materials for applications with a specific lifetime. The lifetime of biodegradable polymers is based on the prediction of their degradation rate, taking into account all of the factors affecting this rate, such as the population of organisms in the environment, the type of polymer or polymers and the chemical structure and environmental conditions. A multitude of these factors and a fundamental understanding of the mechanisms and interactions during degradation, especially in the natural environment, means that at the moment existing models are not sufficiently advanced to be able to clearly determine the lifetime of the end product from biodegradable polymers by one unified theory. [26] The degradation time of polyesters, under conditions conducive to degradation, can be significantly different. Hydrolysis of poly(ε-caprolactone) or polyhydroxyalkanoates can last for months or up to 2-4 years, depending on the molar mass and crystallinity, as opposed to poly (L-lactide), whose hydrolytic degradation occurs for several weeks or up to 5 years in a living organism. However, under industrial composting conditions the biodegradable polymers used fulfilled the degradation time required by EU regulation. [12, 27] In unfavourable conditions, this degradation time can be longer. There are currently challenges

related to the design of materials that are stable in use and at the same time, susceptible to microbial attack during organic recycling. Thus, the main objective of this research on (bio)degradable polymer materials is to determine the degradation conditions during virtual testing. For each polymer application, understanding which materials are optimal for their purpose allows for the accurate prediction of their behaviour and performance over the polymer's lifecycle in real conditions. [23, 28-31] In the case of products with a long-shelf life, such as cosmetics, the use of biodegradable polymers as packaging is still negligible. There are not many different types of (bio)degradable polymers used for this purpose on the market. Therefore, the comprehensive characterisation of complex polymer systems obtained by various methods was undertaken to develop new strategies for selecting appropriate, tailor-made materials for a specific applications as environmentally friendly cosmetic packages. The presented studies compare the degradation of materials obtained by two different extrusion techniques – traditional extrusion method and the 3D printing technology. Among the commercially available biodegradable polymers, those selected for the study were: (i) poly(L-lactide) (semicrystalline polylactide), (ii) blends based on poly(L-lactide) and synthetic poly[(R,S)-3-hydroxybutyrate] (synthetic polyhydroxyalkanoate, an analogue of the biobased one) and a blend based on poly(L-lactide) and bacterial polyhydroxyalkanoate. These polymers possess the correct properties to allow for processing using both traditional extrusion and 3D printing methods and they are also suitable for specific applications. In this instance we have taken into account the potential use of these polymers as cosmetics packaging.

MATERIALS AND METHODS

Materials

The materials used in this study were: (i) poly(L-lactide) 30 μm and 40 μm thick films, a commercial product from NatureWorks LLC, USA that was kindly provided by Pakmar® (NatureWorks® PLA); (ii) PLA and PLA/(R,S)-PHB blends contained 3 mol%, 9 mol%, and 15 mol% of (R,S)-PHB component (calculated using NMR from the intensities of the protons of the methyl groups of the components), PLA, 97PLA/3(R,S)-PHB, 91PLA/9(R,S)-PHB and 85PLA/15(R,S)-PHB were prepared as 300 μm, and in case of PLA also as a 100 μm thick rigid film at the Institute for Engineering of Polymer Materials and Dyes (IMPIB Toruń, Poland) under the MARGEN project [32]; (iii) two commercial 3D printing filaments, PLA filament (Orbi-Tech, Germany) and PLA/PHA blend filament (ColorFabb, The Netherlands) with 88 wt% of PLA the component (determined by TG analysis). The material characterisations have been previously described [33-35].

Fabrication of 3D-printed samples

PLA and PLA/PHA dumbbell-shaped samples, type 1BA (ISO 527 standard [36]) were obtained using a fused deposition modelling printer (FLASHFORGE Dreamer dual extrusion 3D printer). Material preparation and characteristics were described by [35]. PLA and PLA/PHA samples obtained by 3D printing with the crisscross pattern had a thickness of 1.80 ± 0.01 mm and those with a transverse pattern had a thickness of 2.07 ± 0.01 mm.

Hydrolytic degradation under laboratory conditions

For the degradation experiments, the samples were incubated at 70 °C (± 0.5) over a period of 42 days. Degradation experiments were described by [33, 35, 37]. 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 [15]. The molar mass loss was calculated according to [33].

Imaging of sample surfaces

Macroscopic changes to the surface of the samples tested were visualised using a digital camera (Olympus E-410) while microscopic changes were analysed using an optical microscope. These analyses were performed using a Zeiss polarizing microscope (Opton-Axioplan) equipped with a Nikon Coolpix 4500 colour digital camera. Pictures were taken at a magnification of 120x.

Gel permeation chromatography analysis (GPC)

The molar mass and molar-mass dispersity of the samples 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 solvent delivery system with a set of two PL-gel 5 μm MIXED-C ultrahigh efficiency columns (Polymer Laboratories) with a mixed bed and linear range of Mw 200-2000000. An isocratic pump (Spectra Physics 8800) as the solvent delivery system, differential refractive index detector stabilised to a temperature of 35 °C (Shodex SE 61) was applied. 10 μL of 0.5 % m/V sample solution was injected into the system. Polystyrene standards (Calibration Kit S-M-10, Polymer Laboratories) with narrow molar-mass distribution were used to generate a universal calibration curve. The samples were measured using OmniSEC 5.0 (Viscotek) software.

Differential scanning calorimetry (DSC)

The thermal characteristics of the materials were obtained using a TA-DSC Q2000 apparatus (TA Instruments, Newcastle, DE, USA). The instrument was calibrated with high purity in-

dium. 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 °C to 220 °C at a heating rate of 10 °C/min or 20 °C/min. All of the experiments were performed under a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min, using aluminium sample pans. The melting temperature (Tm) was taken as the peak temperature maximum of that melting endotherm, and the glass transition temperature (Tg) was taken as the midpoint of the heat capacity change of the amorphous sample obtained by quenching the melted samples from melt (220 °C).

RESULTS AND DISCUSSION

The degradation experiments of all samples in demineralised water at 70 °C were carried out under laboratory conditions for a period of 42 days. The progress of the hydrolysis of materials was estimated by material examination and failure analysis (macro- and microscopic observations of the samples' surfaces), as well as changes in the specimen's mass and molar mass loss and thermal properties during the performed experiments. There are differences in the rate and the images of degradation of the materials obtained by various methods. There are also differences in the thickness of the materials which affects their properties.

Macroscopic visual evaluation of all the samples tested during the degradation showed erosion as disintegration of the samples (Figure 1).
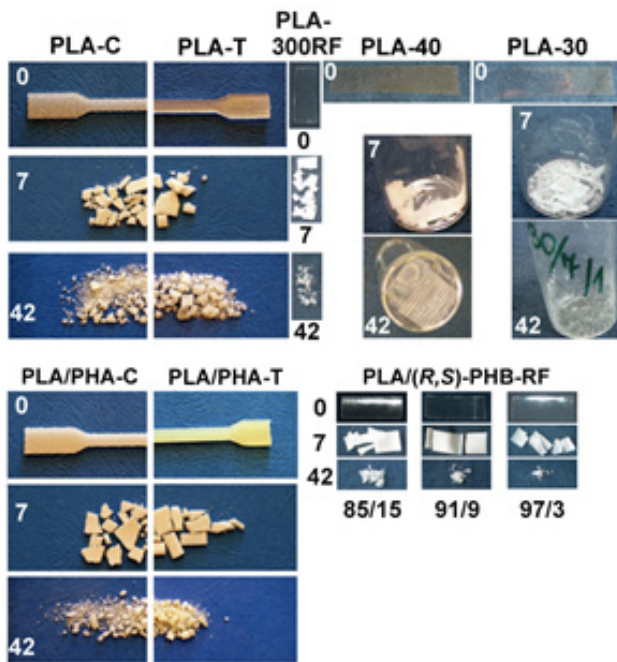

Figure 1: Macrographic images of the PLA and PLA/PHA samples obtained by 3D printing with crisscross (C) and transverse (T) patterns; 300 μm PLA, 97PLA/3(R,S)-PHB, 91PLA/9(R,S)-PHB and 85PLA/15(R,S)-PHB rigid films (RF) as well as 30 μm and 40 μm PLA films obtained by extrusion; before (0) and after 7 and 42 days of hydrolytic degradation test at 70 °C.

Over time, the fragments of the specimens became smaller. Samples of PLA film thinner than 30 μm as well as those printed with crisscross patterns, gave finer fragments. A higher content of (R,S)-PHB in the blend resulted in a prolonged degradation time. Also at the beginning of degradation, the samples were tarnished. Transparent films became milky white and thicker 3D-printed samples changed into a milky whitish-yellow. The decrease in the transparency of all of the studied samples during the degradation results either from molecular reorganisation or from an increase in irregularity due to the accelerated formation of new spherulites [33,34 and references therein].

The use of an optical microscope to monitor the degradation of the PLA-based materials allowed the tracking of changes on the surface of samples. The microscopic observation showed erosion through the cracking and the surface becoming rougher (Figure 2). After a longer period of degradation the degree of crystallinity (see Table 1) and therefore brittleness of the material increased and became stiffer and more susceptible to fractures.
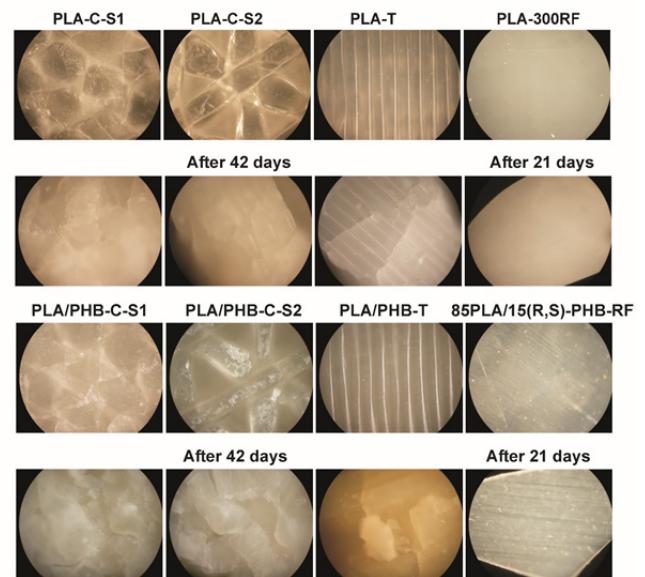

Figure 2: Selected photomicrographs (120x) of two surface layers of PLA and PLA/PHA samples obtained by 3D printing with crisscross (C) and transverse (T) patterns; 300 μm PLA and 85PLA/15(R,S)-PHB rigid films (RF) obtained by extrusion before and after 21 and 42 days of hydrolytic degradation test at 70 °C.

The degradation process in demineralised water resulted in a decrease in the mass of the samples from the beginning of the experiments (Figure 3).

The mass loss of samples proceeds in the following order: PLA films (from the thinnest to the thickest)>PLA/(R,S)-PHB rigid films>3D printed samples, while molar mass loss with opposite order: 300 μm PLA rigid film>3D printed PLA sample with a transverse pattern>100 μm PLA rigid film>3D printed PLA sample with a crisscross pattern>40 μm PLA film>30 μm PLA
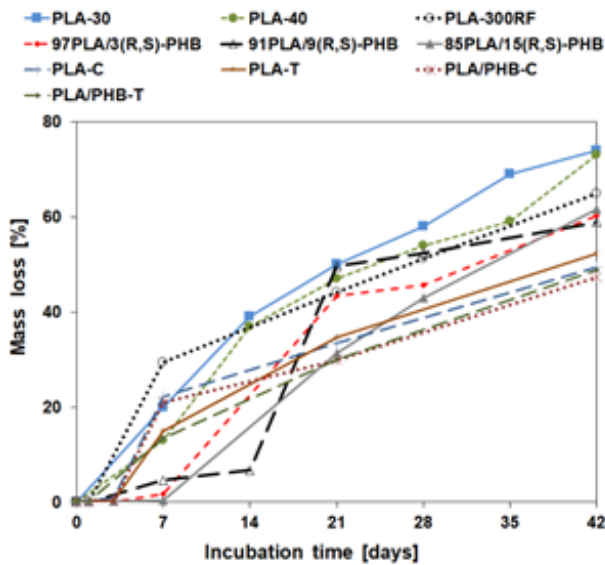
film (Figure 4).

Figure 3: Mass loss of the PLA and PLA/PHA samples obtained by 3D printing with crisscross (C) and transverse (T) patterns; 300 μm PLA, 97PLA/3(*R,S*)-PHB, 91PLA/9(*R,S*)-PHB and 85PLA/15(*R,S*)-PHB rigid films (RF) as well as 30 μm and 40 μm PLA films obtained by extrusion as a function of incubation time during the degradation process at 70 °C.

Figure 4: Number-average molar mass of the PLA samples obtained by 3D printing with crisscross (C) and transverse (T) patterns; the PLA 100 μm and 300 μm rigid films (RF) as well as 30 μm and 40 μm PLA films obtained by extrusion as a function of incubation time during the degradation process at 70 °C.
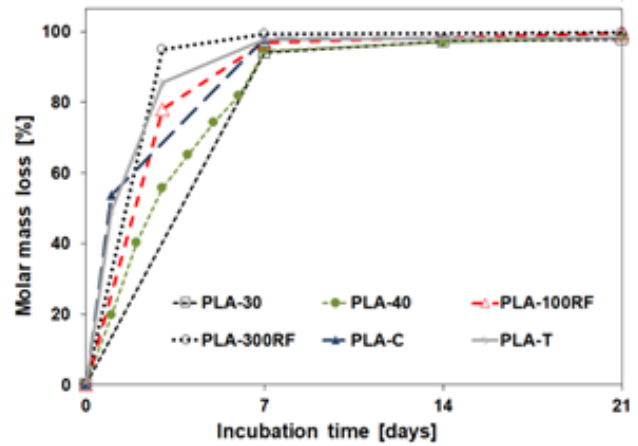
The degradation process for a 300 μm thick rigid PLA film is faster than for the thin 30 μm PLA film. It is well known that sub-millimetre films degrade homogeneously and more slowly (erosion restricted at the surface) than devices with larger sizes. For a thinner film, the degradation products are more easily eluted from the polymer matrix, so mass loss is faster but slower molar mass loss occurs, whereas for a thicker film, the autocatalytic effect occurs and the degradation takes place in the whole polymer matrix. [33, 35 and references therein] It is also worth noting that the presence of a synthetic (*R,S*)-PHB component in the blend delayed the degradation time of the samples tested and lower mass loss was observed compared to PLA samples after the same incubation time. [37]

The thermal properties of the materials during degradation were characterised by differential scanning calorimetry (Table 1).

Table 1: Calorimetric parameters before (0) and after hydrolytic degradation (42 days of incubation) of PLA and PLA/PHA samples obtained by 3D printing with crisscross (C) and transverse (T) patterns at 70 °C, before degradation of the 40 μm PLA film obtained by extrusion (20 °C/min) as well as before (0) and after 21 days of the degradation of the 300 μm 85PLA/15(*R,S*)-PHB rigid film (RF) (10 °C/min).

Sample	PLA-C	PLA-T	PLA-RF	PLA-40	PLA-C	PLA-T
Time [days]	0	0	0	0	42	42
M_w [g/mol]	225,000	223,000	251,000	224,000	N/D	1,900
I-heating run						
T_m [°C]	150.7	150.3	151.6	147.2	128.1	127.5
ΔH_m [J/g]	0.98	1.83	3.7	13.38	49.24	58.30
T_{cc} [°C]	118.0	122.7	128.9	128.2	-	-
ΔH_{cc} [J/g]	-0.93	-1.82	-3.5	-1.03	-	-
II-heating run						
T_g [°C]	62.2	61.7	56.9	58.0	43.3	42.0
Δc_p [J/g°C]	0.50	0.50	N/D	N/D	0.60	0.54
T_m [°C]	-	-	151.6	149.5	126.6	125.8
ΔH_m [J/g]	-	-	3.01	1.33	3.43	1.69
T_{cc} [°C]	-	-	130.2	128.1	110.5	110.5
ΔH_{cc} [J/g]	-	-	-3.0	-1.05	-3.22	-1.67
Sample	PLA/PHA-C	PLA/PHA-T	85PLA/15(*R,S*)-PHB	PLA/PHA-C	PLA/PHA-T	85PLA/15(*R,S*)-PHB
Time [days]	0	0	0	42	42	21

I-heating run						
T_m [°C]	153.5/172.2	154.0/172.6	151.8	123.2/147.0	123.1/147.1	128.6
ΔH_m [J/g]	16.16	11.96	25.38	47.09	58.22	50.76
T_{cc} [°C]	116.5	125.9	99.2	-	-	-
ΔH_{cc} [J/g]	-16.70	-11.79	-22.69	-	-	-
II-heating run						
T_g [°C]	1.9/62.8	1.9/60.4	-2.5/49.7	-9.6/30.5	31.5	33.7
Δc_p [J/g°C]	0.04/0.49	0.04/0.49	N/D	0.03/0.57	0.56	N/D
T_m [°C]	153.4/172.4	152.8/174.5	151.2	114.6/120.3	115.33/120.9	128.1
ΔH_m [J/g]	0.24	0.56	6.61	19.90	22.39	42.35
T_{cc} [°C]	136.8	141.5	126.6	98.1	97.7	85.4
ΔH_{cc} [J/g]	-0.23	-0.53	-4.53	-19.26	-22.07	-42.14

M_w – mass-average molar mass, T_g – glass transition temperature, Δcp – the increment of heat capacity at the glass transition, T_m – melting tempera-ture, ΔH_m – melting enthalpy, T_{cc} – maximum of the exothermic peak of the cold crystallisation temperature, ΔH_{cc} – cold crystallisation enthalpy, N/D – not determined.

Plain PLA samples before degradation showed a higher melting temperature (I-heating run) than the components of the PLA/PHA and 85PLA/15(R,S)-PHB blends. A higher melting point means that there was more heat required to melt it from a solid to a liquid state and blends are more orderly. A melting enthalpy value (ΔH_m) is related to the degree of crystallinity. For plain blends the ΔH_m is also much higher compared to PLA samples. Melting temperature for the plain materials increas-es in the following order: 40 µm PLA film<PLA rigid film and 3D printed PLA samples<85PLA/15(R,S)-PHB, rigid film<3D printed PLA/PHA sample with a transverse pattern>300 µm PLA rigid film>3D printed PLA sample with a crisscross pat-tern. The degradation rate of these samples also proceeds in a similar order because degradation occurs more easily in amor-phous regions (see Figure 4). The maximum of the exother-mic peak of the cold crystallisation temperature (T_{cc}, I-heating run) decreased for the plain PLA samples as follows: 300 µm PLA rigid film and 40 µm PLA film>3D printed PLA sample with transverse pattern>3D printed PLA sample with a crisscross pattern. The chains could begin to freely crystallise at lower temperatures for the crisscross pattern, where the contact time with the printer platform is longer, making the material more orderly. For the blend samples, the lowest T_{cc} was ob-served for 85PLA/15(R,S)-PHB, rigid film where the presence of (R,S)-PHB can not only plasticise but also initiate the crystal-lisation of the blend by induction/nucleation as the nucleation agent (ΔH_{cc} is significantly higher while T_g, and T_{cc} are lower, Table 1). An increase in the cold crystallisation enthalpy with order: 85PLA/15(R,S)-PHB rigid film>3D printed PLA/PHA sam-ple with a crisscross pattern>3D printed PLA/PHA sample with the transverse pattern indicates an increase in the number polymer of chains, especially that of 85PLA/15(R,S)-PHB rigid films that are involved in the crystallisation process, together with a decrease in T_g, which allows the crystallisation to begin at a lower temperature, thus extending its time.

CONCLUSIONS

Ex-ante examination to detect problems and define and mi-nimise the potential failure of novel polymer products before they arise is essential for the forensic engineering of advanced polymeric materials. The performed studies have shown that the processing conditions lead to different thermal and me-chanical interactions with the material, as well as causing changes to the material's properties during degradation. The beginning of disintegration and the way in which the samples disintegrate depends not only on the shap of the material, but also on the way it is obtained. The type of process and the contact time with higher temperatures during processing plays a significant role. With the extension of the degradation time, the degree of crystallinity, and thus the brittleness of the material increased and it becomes stiffer and more sus-ceptible to fractures, in addition the surface becomes rougher and tarnished. It should be also remembered that PLA-based materials are degraded with the autocatalytic effect and deg-radation is depend on the thickness of the material.

AUTHOR CONTRIBUTIONS

This manuscript was written through the contributions of all authors. Joanna Rydz contributed 60 %, while the other au-thors contributed within 40 % equally. All authors have given approval to the final version of the manuscript.

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