Title: (BIO)DEGRADABLE POLYMERIC MATERIALS FOR A SUSTAINABLE FUTURE- PART 1. ORGANIC RECYCLING OF PLA/PBAT BLENDS IN THE FORM OF PROTOTYPE PACKAGES WITH LONG SHELF-LIFE

Article Type: Full Length Article

Keywords: organic recycling, biodegradation, hydrolytic degradation, packages, poly(butylene adipate-co-terephthalate), polylactide, talc

Abstract: Prediction studies of advanced (bio)degradable polymeric materials are crucial when their potential applications as compostable products with long shelf-life is considered for today's market. The aim of this study was to determine the effect of the polylactide (PLA) content in the blends of PLA and poly(butylene adipate-co-terephthalate) (PBAT); specifically how the material's thickness corresponded to changes that occurred in products during the degradation process. Additionally, the influence of talc on the degradation profile of all samples in all environments was investigated. It was found that, differences in the degradation rate of materials tested with a similar content of the PLA component could be caused by differences in their thickness, the presence of commercial additives used during processing or a combination of both. The obtained results indicated that the presence of talc may interfere with materials behaviour towards water and consequently alter their degradation profile.
Zabrze, 12.04.2018

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Dear Editor in Chief

Please find enclosed the revised manuscript of our paper entitled “(Bio)degradable polymeric materials for a sustainable future- part 1. Organic recycling of PLA/PBAT blends in the form of prototype packages with long shelf-life” and our comments to the remarks of the reviewer. We would like to thank for the detailed reviewing of the manuscript. We have made our best in order to improve the paper in accordance with the pertinent reviewer comments.

We hope that the corrected version of our manuscript meets your expectations and will be acceptable for publication.

Kind regards,

Marta Musioł
**Detailed Response to Reviewers**

<table>
<thead>
<tr>
<th>Reviewer #4 Comment</th>
<th>Author's Response</th>
<th>Revised Text</th>
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<tr>
<td>1. For the expression of highlights, the authors should state the novelty of their study. However, the four points seem more like a statement of experimental results rather than the novelty of the study.</td>
<td>Highlights were corrected</td>
<td>Revised manuscript</td>
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<tr>
<td>2. Line 28, Abstract: “Therefore” in this sentence is not correctly used.</td>
<td>Abstract was reworded and corrected</td>
<td>Additionally, the influence of talc on the degradation profile of all samples in all environments was investigated. It was found that, differences in the degradation rate of materials tested with a similar content of the PLA component could be caused by differences in their thickness, the presence of commercial additives used during processing or a combination of both. Page 1 Lines 19-24 in new submission</td>
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<td>3. The standard deviation was not contained in the data shown in Tables 1 &amp; 2.</td>
<td>Tables 1 and 2 were corrected</td>
<td>Page 4 Line 115 and page 9 Line 281 in new submission</td>
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<tr>
<td>4. Line 49: Delete &quot;being&quot; 5. Line 50: Change both &quot;were&quot;s to &quot;are&quot;</td>
<td>Corrected</td>
<td>According to PlasticsEurope and European Bioplastics, nova-Institute, the amount of global plastic production in 2017 was estimated at 340 million tonnes, of this amount 2.05 million tonnes are biobased plastics and 880 000 tonnes are biobased biodegradable polymers (Report European Bioplastics, 2017). Page 2 Lines 47-51 in new submission</td>
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<td>6. Lines 83-85: The sentence is not correct.</td>
<td>Corrected</td>
<td>Additionally, PBAT is processable on conventional blow film plants applied for low-density polyethylene what can contribute to the reduction of the cost of producing the material (Plasticsportal.net) Page 3 Lines 84-86 in new submission</td>
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<td>7 Lines 276-277: &quot;which may suggest that the autocatalytic effect of the hydrolytic degradation for this sample occurred.” Do you have any reference to support this explanation?</td>
<td>Corrected</td>
<td>…which may suggest that the autocatalytic effect of the hydrolytic degradation for this sample occurred. (Espartero et al. 1996). Page 9 Line 275 in new submission</td>
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(BIO)DEGRADABLE POLYMERIC MATERIALS FOR A SUSTAINABLE FUTURE-
PART 1. ORGANIC RECYCLING OF PLA/PBAT BLENDS IN THE FORM OF
PROTOTYPE PACKAGES WITH LONG SHELF-LIFE

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Highlights:

Degradation behavior of packaging with commercial additives has been investigated.
The talc greatly influences on the packaging water absorption and degradation profile.
Talc may cause differences in water absorption depending on environment humidity.
The influence of samples’ shape on the degradation profile has been confirmed.
The shelf life of the product can be adjusted by quantity of the commercial additive.
Abstract

Prediction studies of advanced (bio)degradable polymeric materials are crucial when their potential applications as compostable products with long shelf-life is considered for today’s market. The aim of this study was to determine the effect of the polylactide (PLA) content in the blends of PLA and poly(butylene adipate-co-terephthalate) (PBAT); specifically how the material’s thickness corresponded to changes that occurred in products during the degradation process. Additionally, the influence of talc on the degradation profile of all samples in all environments was investigated. It was found that, differences in the degradation rate of materials tested with a similar content of the PLA component could be caused by differences in their thickness, the presence of commercial additives used during processing or a combination of both. The obtained results indicated that the presence of talc may interfere with materials behaviour towards water and consequently alter their degradation profile.

Keywords: organic recycling, biodegradation, hydrolytic degradation, packages, poly(butylene adipate-co-terephthalate), polylactide, talc

1. Introduction

The key to achieving success and increased presence in the bioeconomy industry is to understand both the advantages and limitations of biodegradable and biobased products. Biodegradable polymers are now the material of choice due to the plastics industry needing to change their strategy as a result of years of pollution. This influence has become the steady
driving force behind the manufacturing sector in Europe over the last few years (Rydz et al., 2018). Conventional polymers available today are thought to have many advantages, such as good processability, hydrophobicity and having excellent barrier properties. However, these materials are characterised by high resistance to biological agents and the widespread use of them for packaging has made them the cause of an array of environmental problems. Plastic waste deposited in landfills occupies more new areas of ground each year and even threatens our oceans. One of the ways to solve this growing problem is to introduce and promote the consistent usage of packaging made from natural or biodegradable polymers into the market (Ghanbarzadeh and Almasi, 2013; Sam et al., 2016; Narodoslawsky et al., 2015).

Biodegradable packages with special marks or indicators could be separated from the municipal waste stream and directed into organic recycling. This could be achieved by collecting them together with the organic waste arising from households (Höglund et al., 2012; Kale et al., 2006, 2007a; Musiół et al., 2015; Sikorska et al., 2008, 2012; Swift, 2015). According to PlasticsEurope and European Bioplastics (nova-Institute) the amount of global plastic production in 2017 was estimated at 340 million tonnes; of this amount 2.05 million tonnes are biobased plastics and 880 000 tonnes are biobased biodegradable polymers (Report European Bioplastics, 2017). Therefore, it is extremely important to increase consumer awareness about biodegradable polymeric materials and introduce them to the market, so biodegradable packaging will become an integral part of their lives. The global introduction of biodegradable polymeric materials for packaging must be preceded by a number of changes, such as the development of new technology, the improvement of the infrastructure of composting, as well as the financial capacity and the appropriate policies that are required (DSTI/STP/BIO(2013)6/FINAL, 2013; Shahzad et al., 2017; Narodoslawsky, 2010; Koller et al., 2017). Thus, research, especially proof of concept studies, in this area are still required.

The value chain of biodegradable polymeric materials comes from the production of polymers through to the consumer and then through waste management (PLASTICE project) and research should be carried out at every link of this chain.

The term biodegradable is used to describe those materials, which are degraded by the enzymatic action of microorganisms (bacteria and fungi). Biodegradation can occur under aerobic and anaerobic conditions. The final degradation products of the process under aerobic conditions are CO₂, H₂O and biomass (Adamus et al., 2006; Sikorska et al., 2015). The literature reviewed indicates that aliphatic polyesters are now considered potential biomaterials for applications in agriculture, medicine, pharmacy and packaging (Rydz et al., 2015a; Sikorska et al., 2014; Musiół et al., 2016a, 2016b). PLA exhibits a high tensile
modulus, resistance to UV radiation and fats, and the ability to be processed by conventional methods (Ahmed and Varshney, 2011; Ingaro et al., 2015; Jabeen et al., 2015; Kale et al., 2007b, Jost and Kopitzky, 2015). However, there are several examples where PLA-based materials did not meet the requirements as a packaging material, especially for long shelf-life products (Rydz et al., 2013a, 2013b, 2015b). Aliphatic-aromatic copolyesters can be applied in package production due to the good functionality of their aromatic polyesters and the biodegradability of aliphatic polyesters (Witt et al., 2001; Rychter 2006, 2010, 2011; Żenkiewicz et al., 2013).PBAT is a linear statistical aliphatic-aromatic copolyester consisting of 1,4-butadiol and terephthalic acid monomers as rigid units and 1,4-butadiol and adipic acid monomers as flexible units. PBAT with the content of terephthalic acid higher than 35 mol% has better mechanical and thermal properties (Siyamak et al., 2012; Bohlmann, 2005). However, the increase of its content is followed by a significant decrease in the biodegradation rate as the growing amount of aromatic units elevates resistance against microorganisms (Vroman and Tighzert, 2009; Kijchavengkul et al., 2010). On the market, BASF (Ecoflex®) and Novamont (Origo-Bi™, former Eastar-Bio™/Eastman with 30-70 % renewable content) PBAT producers are widely known (Jiang and Loos, 2016; News/Press releases, 2013a, 2013b). Additionally, PBAT is processable on conventional blow film plants applied for low-density polyethylene what can contribute to the reduction of the cost of producing the material (Plasticsportal.net). The PBAT copolyester is used commercially in food packaging, as an agricultural plastic and it is also used in sporting goods. Recent studies have shown that an aliphatic-aromatic copolyester and polylactide commercial blend demonstrates good stability during aging in cosmetic simulants, which is important for prospective applications of this polymeric material as compostable packing for products with a long shelf-life (Sikorska et al., 2017).

2. Materials and Methods
This paper presents a (bio)degradation study of PLA and PBAT blends in the form of prototype packages with long shelf-life. The biodegradation tests were performed under industrial composting conditions in a pile and in a container system. Additionally, an abiotic degradation test was carried out under laboratory conditions. The selected materials allowed the determination of the effect of PLA content (17 and 40 mol%) in the films on their degradation process and a comparison of the degradation of materials with different thickness and the same molar content (40 mol%) of PLA. The changes of molar mass, molar-mass dispersity, composition and thermal properties of the samples were observed during an
incubation period in degradation media and the resultant material was characterised by GPC, 
$^1$H NMR, TGA and DSC techniques, respectively.

2.1. Materials

The case study on organic recycling was performed with prototype materials prepared by 
blowing (blends of PBAT with PLA) containing 17 and 40 mol% of PLA into films (marked 
respectively as F/17 and F/40) and 40 mol% of PLA in form of disposable bags (marked as 
T/40). The samples were prepared by the Bioerg Company in Poland, by extrusion to produce 
on test stands of conventional flat proportions using a single-screw extruder. The technical 
details concerning the materials, additives and processing methods are commercially 
protected. Table 1 presents the description of plain samples before degradation tests.

Table 1. Plain materials studied – prototype products of Bioerg Company, Poland

2.2. Environments

The comparative (bio)degradation studies of blends in the form of films and disposable bags 
were conducted under industrial composting conditions in two systems: a static composting 
open-air pile and a KNEER container system. The abiotic degradation in distilled water at 70 
ºC was performed to indicate that the control of both moisture and temperature is an 
important factor that affects the degradation of the investigated materials.

2.2.1. (Bio)degradation test under industrial composting conditions

The composting process was carried out at the Mechanical-Biological Waste Treatment 
Station in Zabrze (Upper Silesia, Poland) in a static composting open-air pile (located at: 
latitude 50º 18’ 30,71” N and longitude 18º 48’ 18,52” E) in a KNEER container system, as 
described by Musiol et al., 2011. In the composting pile, samples were incubated for 21 days 
at an average temperature of 61 ºC (± 5 ºC) with an average pH of 6.9. The samples were run 
in triplicate and the experiments were conducted between September and October 2015. In the 
container system, the samples were incubated for 21 days in three cages at an average 
temperature of 60 ºC (± 5 ºC) with an average pH of 7.5. The cages with the materials studied 
were placed into composting systems at a depth of 1 meter below the compost surface.
2.2.2. Abiotic degradation test under the laboratory conditions

The samples were incubated in distilled water at 70 °C over a period of 70 days, according to norm ISO (International Standard: ISO 15814). The samples were inserted into 30-mL screw-capped vials, containing 25 mL of medium, and then placed in a laboratory oven at 70 °C. The samples were each run in triplicate. After a specified time of incubation the samples were removed from the vials and cleaned by washing in distilled water, they were then drained on blotting paper and then dried to a constant mass under a vacuum at 25 °C.

2.3. Measurements

2.3.1. Gel Permeation Chromatography (GPC) analysis

The GPC experiments for the PLA/PBAT samples were conducted as described previously by Sikorska et al. (2015).

2.3.2. $^1$H nuclear magnetic resonance (NMR) spectroscopy

$^1$H NMR spectra were recorded using a Bruker-Advance spectrometer as described by Rydz et al., (2015b). The blend composition was determined based on the integration of protons from the methine group of the PLA component (at $\delta = 5.20$ ppm) and protons of the methylene group in the aromatic and aliphatic dyads of the PBAT component (region between $\delta = 4.0$ to 4.5 ppm) (Rychter et al., 2010).

2.3.3. pH measurement

The pH measurements of the compost according to norm (PN-Z-15011-3:2001) were carried out as described previously by Sikorska et al. (2015).

2.3.4. Imaging of sample surfaces

Macroscopic changes in the surface of the materials tested were visualised using a digital camera (Olympus E-410), while microscopic changes were analysed using an optical microscope and a scanning electron microscope (SEM). Optical analysis was performed using a Zeiss polarizing microscope (Opton-Axioplan) equipped with a Nikon Coolpix 4500 colour digital camera. Pictures were taken at a magnification of 100x. SEM/EDS studies were performed using of a Quanta 250 FEG (FEI Company, USA) high resolution environmental SEM operated at 10 kV acceleration voltages. The samples were observed without a coating, under low vacuum (80 Pa) conditions using a backscattered electron (BSE) detector. Energy
dispersive X-ray spectroscopy (EDS) was used for analysis of elemental composition. The spectra were collected by an EDAX Apollo SDD spectrometer with Genesis V6.20 software.

2.3.5. Thermal properties
Thermal analysis was carried out on a Mettler-Toledo TGA/DSC STARRe System, from 25 to 800 °C at a heating rate of 10 °C/min, under a constant flow of 60 mL/min of nitrogen. The obtained TGA data were analysed using the Mettler-Toledo Star System SW 9.30.
Thermal characteristics of the materials studied were also obtained using a TA DSC 2010 apparatus (TA Instruments, New Castle, DE). The first calorimetric trace (I-scan, preliminary heating run) in which the thermal history was suppressed, were acquired from -80 °C to 200 °C at a heating rate of 20 °C/min, under a nitrogen atmosphere (flow rate = 50 mL/min). The instrument was calibrated with indium and gallium standards. The melting temperature ($T_m$) was taken as the peak maximum of the melting endotherm.

2.3.6. Measurement of the contact angle
Contact angle measurements (Q) for the tested material’s surface properties were measured statically using a contact angle goniometer CAM101 (KSV Instruments). The water contact angles were determined in air using the sessile-drop method. A series of images for the water drops (3 µL) were acquired during 15 s, and the average contact angle value was calculated. The contact angle measurements were performed on dry surfaces at 20 °C. An average of five values of contact angles from different parts of the samples was calculated. Two samples of each surface were used for measurements.

3. Results and Discussion
(Bio)degradation studies were conducted for prototype products made by the Bioerg Company, Poland. The changes of the surface and the changes of the average molar mass of samples (determined by GPC) are indicators of the degradation progress. The thermal characteristics of the materials during the degradation process were determined by TGA and DSC results. These outcomes led to important findings about the changes in the thermal properties, crystallinity and thermal stability. The SEM studies enabled the identification of the additives in the samples based on chemical composition (Bart JCJ, 2006).
Macro- and microscopic visual evaluation of the samples during the degradation process indicated erosion as well as tarnishing of the film’s surface beginning from the 21st day of
incubation in both composting systems. This observation is easy to see especially in the
microscopic images shown in Fig 1. After 21 days of degradation the deterioration of the
investigated films, F/17 and F/40 samples in the composting pile and containers began to
crack. Disintegration of the film samples also began after 21 days of the reference abiotic
degradation tests. Both films with 17 and 40 % of PLA in their blends during degradation
showed similar morphological changes that occurred predominately on the sample surface.
The thicker T/40 samples showed little change for 21 days, only the discoloration of samples
that were placed in direct contact with compost was noticed (Fig. 1).

**Fig. 1.** Selected macro- (A) and microscopic (B) images of samples before (0) and after 21
days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.

The observed changes of the samples incubated in water and both composting systems: pile
and containers, confirmed the fastest deterioration of thin films was with 17 % content of
PLA in the blend (F/17) while the slowest were the second film that contained 40 % content
of PLA in the blend (F/40) and the thickest sample of the final product with the same content
of PLA (T/40).
The SEM micrographs of all investigated samples indicated the presence of white inclusions
in the polymeric matrix (Fig. 2). The energy-dispersive spectroscope (EDS) scan analysis of
selected regions showed the presence of Mg and Si which has most likely originated from a
commercial additive, hydrated magnesium silicate \( \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \) (talc). Talc powder is
often used as a dye and a filler, also used in the food industry (food additive number E553b)
(Whaling et al. 2006, Commission delegated regulation (eu) no 1363/2013).

**Fig. 2.** Selected scanning electron microscopy with microanalysis (SEM-EDS) micrograph of
plain T/40 sample surface at a magnification of 2500x.

Talc shows the dichotomy of wetting properties independent of relative humidity (RH). At
low RH water adsorbs readily on the surface of talc because adhesive interactions in talc are
strong enough. However, at saturation the water-water interactions (cohesion) overcome talc
adhesion and thus water beads up on its surface (Rotenberg et al. 2011). The comparison of
average contact angle values (78.74, 83.79 and 96.14 for F/17, F/40 and T/40 respectively)
confirmed that the T/40 surface was the most hydrophobic with the highest contact angle
value and the most stable of the drops during the longer contact with the examined surfaces.

On the contrary, in the case of F/17 and F/40 samples, a drop of water left on the surface for the same time (longer than the measurement time) reduced the contact angle value by up to several degrees and it was probably caused by the influence of talc. Thus, the presence of talc in all of the samples may have disturbed their behavior towards water and consequently altered the degradation profile.

The reliable monitoring of the sample’s mass changes during the degradation process under industrial composting conditions was impossible. Thus Fig. 3 presents the only mass changes of materials that occurred during the incubation in distilled water at 70 °C.

**Fig. 3.** The mass changes of materials studied during the abiotic degradation testing at 70 °C.

Systematic remaining mass decrease was found in all of the studied samples. At the beginning of degradation, the mass of blends decreased slightly with a more noticeable molar mass loss (Fig. 3 and Fig. 4), which is typical for the hydrolytic degradation mechanism (Rydz et al., 2013). It is well known that the degradation of PLA in an aqueous environment occurs through the hydrolysis of ester bonds, which increases the amount of carboxy end-groups (-COOH) and generates the autocatalytic effect (Espartero et al. 1996). At the initial stage, the biggest mass loss was observed for thin film samples with a higher content of the PLA component in the blend, F/40. The mass loss for the thicker sample, with 40 % PLA, (T/40) began later but at the end of the degradation it reached the highest volume. It is important to notice that PLA shows lower absorption of water in blends than the second component PBAT (Osman et al. 2014, Willett et al. 2002) and the presence of talc in all of the samples could had an influence on water absorption. The TG analysis shows that the amount of residue is 7, 8 and 15 % for F/17, F/40 and T/40 samples, respectively. This implies a higher quantity of talc in the T/40 sample. Additionally, at the beginning of the incubation for thick T/40 samples the degradation products could be closed inside the polymeric matrix which is consistent with the mechanism of autocatalytic hydrolysis proposed by Vert (Espartero et al. 1996).

The degradation process in all environments resulted in a decrease of the average molar mass of the investigated samples but at a different rate (Fig. 4).
Fig. 4. The changes in molar mass of the investigated samples before degradation (0) and after 21 days of incubation in: C - container, H - distilled water at 70 °C.

After 21 days of incubation (Fig. 4) the comparable shifting of the monomodal traces to the higher retention volume values was observed for all of the investigated samples. However, this phenomenon was more visible for the thicker T/40 sample after incubation in distilled water, which may suggest that the autocatalytic effect of the hydrolytic degradation for this sample occurred (Espartero et al. 1996). What was also evidenced by an increase in the molar-mass dispersity.

On the basis of $^1$H NMR spectra the PLA/PBAT composition changes appearance during the degradation in all environments, after 21 days incubation, were calculated and are presented in Table 2 (Rychter et al., 2010).

Table 2. The changes of PLA content (mol%) of samples incubated for 21 days in different environmental conditions, calculated from 1H NMR spectra.

Slight changes in the blend composition were observed from the beginning of the incubation in distilled water. This suggests that the degradation of both components in all of the materials studied under these conditions occurs at almost the same rate until the 21st day of the degradation test, and only after that, the largest difference started to appear. The total reduction of the PLA component of the thin sample (F/17) was observed after 42 days of the abiotic degradation test under the conditions given and for the thicker sample (T/40), after 70 days of the process. This phenomenon is not observed for the thin film sample F/40 with the same amount of PLA, in which the 15 mol% of PLA after 70 days of degradation in distilled water is still present (Yang et al. 2005). This result also confirms the contribution of the autocatalytic effect during the hydrolytic degradation in distilled water occurring in the T/40 sample. For the F/17 sample, the decrease of PLA content under composting conditions is higher than during the degradation in distilled water at 70 °C after the same time period (see Table 2). Rychter et al. (2010) showed that the mechanism of PBAT degradation in the standardised, sandy soil proceeds enzymatically. This may suggest that under industrial composting conditions this mechanism for PBAT as the blend component may have an impact on the degradation process. In the container system, the more favourable conditions for enzymatic degradation exists, thus leaching of PLA degradation products from the blend is
facilitated by the degradation of PBAT. Moreover, Oyama et al. (2011) indicated that the products of PLA degradation catalyzes the hydrolytic degradation of the PBAT component in the blend. This conclusion points out that for the blend with a lower content of PLA, a lower hydrolytic degradation rate of PBAT is observed and it results in a lower decrease of $M_n$ during incubation in a container (see Fig. 4). In the case of materials with higher PLA content such as F/40 and T/40 samples, the observed higher $M_n$ changes suggests hydrolytic degradation of both blend components. The obtained results and the composition changes suggest the hydrolytic degradation of both components under composting conditions. Thus, in the case of the F/17 sample, the enzymatic degradation of PBAT, especially in the container, may play an important role. Moreover, the changes of the blend composition observed during the degradation process under industrial composting conditions suggests that the degradation of the blend components are more rapid in the container system than in composting pile. This is probably caused by the higher humidity level of the compost in the container system. The static composting pile with natural aeration, located in the open area, is exposed to all weather conditions, which can affect the composting process. In opposition to this, the composting process in the closed system is independent of weather conditions and it allows for better control of the process than in open systems (Kale et al., 2007a). The behavior of the investigated materials during the degradation process in different environments was characterised using thermogravimetric analysis. The first differential TGA curve (DTG thermograms) obtained for the materials after 21 days of incubation are plotted in Fig. 5.

**Fig. 5.** First differential TGA curve of investigated materials before (0) and after 21 days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.

The thermal effects of both components in the investigated blend samples are similar to each other. This may suggest that these effects partially overlap, which is more visible in the samples with higher PLA content. After degradation in all environments for the thicker sample (T/40) in the part of the curve in the low temperature region, which corresponds to the PLA, a broader DTG peak than for F/40 was observed. This result confirms the participation of the autocatalytic effect in the T/40 sample’s degradation process (Espartero et al. 1996). After the degradation of all the investigated samples in the container system the changes in the DTG peak, which corresponds to the PBAT component, was also observed. This indicated
that the conclusions, based on the changes in the composition and molar masses of the enzymatic mechanism of PBAT degradation under these conditions are correct with minor contributions of hydrolytic degradation of the investigated material, depending on the PLA content and/or the presence of talc in the samples (Rychter et al., 2010).

The DSC results presented in Fig. 6 suggests that the samples studied are not compatible. All the DSC thermograms showed two broad peaks with the maximum value corresponding to both PLA and PBAT component’s melting temperatures.

**Fig. 6.** DSC plot of the investigated materials before (0) and after 21 days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.

It is apparent from the DSC traces of the F/40 and T/40 samples after degradation under industrial composting conditions that the melting peak, which corresponds to PLA, is well defined. This result suggests that after degradation in these conditions, more crystalline solid domains with regular crystals were obtained, which in turn results in a sharper melting peak, meaning the material goes from solid to liquid in a very short temperature range (Lucas et. al 2008). After degradation in distilled water at 70 °C the PLA melting peak is more expanded. The observed changes in this region for all of the samples could result from the presence of the shorter polymer chains formed *via* the hydrolysis of ester bonds and/or the formation of small crystals with irregular structures existing in rigid amorphous domains (Iannace et al. 2001). For the F/17 sample after degradation in the container system, this phenomenon is also observed. This may suggest that under these conditions the regular crystals cannot be properly formed because of the faster leaching of low molar mass PLA oligomers to the degradation medium, which could be facilitated by the degradation of PBAT, as was described above.

**4. Conclusion**

The obtained results indicate that both components of the blend are degraded, but at different rates. The differences in the degradation rate of the materials tested, with a similar content of the PLA component, could be caused by differences in their thickness and/or the presence of commercial additives used during the processing stage. The use of a larger quantity of talc in the production of disposable bags may cause differences in the water absorption of polymeric materials depending on the degradation environment humidity. Additionally, in the case of the
sample of thin film with a lower content of PLA (17 mol%), besides hydrolysis, enzymatic
degradation in the container system probably occurred. Therefore, in order to precisely
determine the performance parameters of final products, all factors need be considered,
because even if we use materials of the same composition, but with differences in their
thickness or thermal and processing history, they may not behave in the same way during
usage.

Acknowledgements

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products.

Author Contributions

This manuscript was written through contributions from all authors. Marta Musiol contributed
80%, Wanda Sikorska contributed 15%, while other authors within 5% contributed equally
to this work. All authors have given approval to the final version of the manuscript.
**Literature**

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Environ. 537, 385-398.


Plasticsportal.net Original – the certified compostable polymer ecoflex®
https://www.plasticsportal.net/wa/plasticsEU~ro_RO/portal/show/content/products/biodegradable_plastics/ecoflex, accessed 27.03.2018


Rychter, P, Biczak, R., Herman, B., Smyła, A., Kurcok, P., Adamus, G., Kowalczuk, M., 2006. Environmental degradation of polyester blends containing atactic poly(3-


commercial blends in view of potential applications as compostable cosmetic packages. Polymers 9(7), 257.


Prediction studies of advanced (bio)degradable polymeric materials are crucial when in view of their potential applications as compostable products with long shelf-life is considered for today’s market. The aim of this study was to determine the effect of the polylactide (PLA) content in the blends of PLA and poly(butylene adipate-co-terephthalate) (PBAT) blends; specifically how the material’s thickness corresponded to changes that occurred in products during the degradation process. Additionally, the influence of talc on the degradation profile of all samples in all environments was investigated. It was found that, differences in the degradation rate of materials tested with a similar content of the PLA component could be caused by differences in their thickness, and/or the presence of commercial additives used during processing or a combination of both. Therefore, the influence of talc on the degradation rate of all samples in all types of environments was investigated. The obtained results indicated that the presence of talc may interfere with their materials behaviour towards water and consequently alter their degradation profile.

Keywords: organic recycling, biodegradation, hydrolytic degradation, packages, poly(butylene adipate-co-terephthalate), polylactide, talc

1. Introduction

The key to achieving success and increased presence in the bioeconomy industry is to understand both the advantages and limitations of biodegradable and/or biobased products.
Biodegradable polymers are now the material of choice due to the plastics industry needing to change their strategy as a result of regarding the environmental consequences after years of pollution. This influence has become the steady driving force behind the manufacturing sector in Europe over the last few years (Rydz et al., 2018). Conventional polymers available today are thought to have many advantages, such as good processability, hydrophobicity and having excellent barrier properties. However, these materials are characterized by high resistance to biological agents and the widespread use of them for packaging has made them the cause of an array of environmental problems. Plastic waste deposited in landfills occupies more new areas of ground each year and even threatens our oceans. One of the ways to solve this growing problem is to introduce and promote the consistent usage of packaging made from natural or biodegradable polymers into the market (Ghanbarzadeh and Almasi, 2013; Sam et al., 2016; Narodoslawsky et al., 2015). Biodegradable packages with special marks or indicators could be separated from the municipal waste stream and directed into organic recycling. This could be achieved by collecting them together with the organic waste arising from households (Höglund et al., 2012; Kale et al., 2006, 2007a; Musiół et al., 2015; Sikorska et al., 2008, 2012; Swift, 2015). According to PlasticsEurope and European Bioplastics; the amount of global plastic production in 2017 was estimated at being 340 million tonnes; of this amount 2.05 million tonnes were biobased plastics and 880 000 tonnes are biobased biodegradable polymers (Report European Bioplastics, 2017). Therefore, it is extremely important to increase consumer awareness about biodegradable polymeric materials and introduce them to the market, so biodegradable packaging will become an integral part of their lives. The global introduction of biodegradable polymeric materials for packaging must be preceded by a number of changes, such as the development of new technology, the improvement of the infrastructure of composting, as well as the financial capacity and the appropriate policies that are required (DSTI/STP/BIO(2013)6/FINAL, 2013; Shahzad et al., 2017; Narodoslawsky, 2010; Koller et al., 2017). Thus, research, especially proof of concept studies, in this area are still required.

The value chain of biodegradable polymeric materials comes from the productions of polymers through to the consumer and then through waste management (PLASTICE project) and. Research activities should be carried out at every link of this chain.

The term biodegradable is used to describe those materials, which are degraded by the enzymatic action of microorganisms (bacteria and fungi). Biodegradation can occur under aerobic and anaerobic conditions. The final degradation products of the process under aerobic conditions are CO₂, H₂O and biomass (Adamus et al., 2006; Sikorska et al., 2015). The
literature reviewed indicates that aliphatic polyesters are now considered as—potential biomaterials for applications in agriculture, medicine, pharmacy and packaging (Rydz et al., 2015a; Sikorska et al., 2014; Musioł et al., 2016a, 2016b). PLA exhibits a high tensile modulus, resistance to UV radiation and fats, and the ability to be processed by conventional methods (Ahmed and Varshney, 2011; Ingaro et al., 2015; Jabeen et al., 2015; Kale et al., 2007b, Jost and Kopitzky, 2015). However, there are several examples where PLA-based materials did not meet the requirements as a packaging material, especially for long shelf-life products (Rydz et al., 2013a, 2013b, 2015b). Aliphatic-aromatic copolyesters can be applied in package production due to the good functionality of their aromatic polyesters and the biodegradability of aliphatic polyesters (Witt et al., 2001; Rychter 2006, 2010, 2011; Żenkiewicz et al., 2013).

PBAT is a linear statistical aliphatic-aromatic copolyester consisting of 1,4-butanediol and terephthalic acid monomers as rigid units and 1,4-butanediol and adipic acid monomers as flexible units. PBAT with the content of terephthalic acid higher than 35 mol% has better mechanical and thermal properties (Siayamak et al., 2012; Bohlmann, 2005). However, the increase of its content is followed by a significant decrease in the biodegradation rate as the growing amount of aromatic units elevates resistance against microorganisms (Vroman and Tighzert, 2009; Kijchavengkul et al., 2010). On the market, BASF (Ecoflex®) and Novamont (Origo-Bi™, former Eastar-Bio™/Eastman with 30-70 % renewable content) PBAT producers are widely known (Jiang and Loos, 2016; News/Press releases, 2013a, 2013b).

Additionally, PBAT is processable on conventional lines—blow film plants applied for low-density polyethylene that can be used for processing PBAT and from that point it what can contribute to the reduction of the cost of producing the material (Plasticsportal.net). The PBAT copolyester is used commercially in food packaging, as an agricultural plastic and it is also used in sporting goods. Recent studies have shown that the aliphatic-aromatic copolyester and polylactide commercial blend demonstrates good stability during aging in cosmetic simulants, which is important for prospective applications of this polymeric material as compostable packing for products with a long shelf-life (Sikorska et al., 2017).

2. Materials and Methods

This paper presents a (bio)degradation study of PLA and PBAT blends in the form of prototype packages with long shelf-life. The biodegradation tests were performed under industrial composting conditions in a pile and in a container system. Additionally, an abiotic degradation test was carried out under laboratory conditions. The selected materials allowed
the determination of the effect of PLA content (17 and 40 mol%) in the films on their degradation process and a comparison of the degradation of materials with different thickness and the same molar content (40 mol%) of PLA. The changes of molar mass, molar-mass dispersity, composition and thermal properties of the samples were observed during an incubation period in degradation media and the resultant material was characterized by GPC, $^1$H NMR, TGA and DSC techniques, respectively.

2.1. Materials

The case study on organic recycling was performed with prototype materials prepared by blowing (blends of PBAT with PLA) containing 17 and 40 mol% of PLA into films (marked respectively as F/17 and F/40) and 40 mol% of PLA in form of disposable bags (marked as T/40). The samples were prepared by the Bioerg Company in Poland, by extrusion to produce on test stands of conventional flat proportions using a single-screw extruder. The technical details concerning the materials, additives and processing methods are commercially protected. Table 1 presents the description of plain samples before degradation tests.

Table 1. Plain materials studied – prototype products of Bioerg Company, Poland

2.2. Environments

The comparative (bio)degradation studies of blends in the form of films and disposable bags were conducted under industrial composting conditions in two systems: the static composting open-air pile and a KNEER container system. The abiotic degradation in distilled water at 70 ºC was performed to indicate that the control of both moisture and temperature is an important factor that affects the degradation of the investigated materials.

2.2.1. (Bio)degradation test under industrial composting conditions

The composting process was carried out at the Mechanical-Biological Waste Treatment Station in Zabrze (Upper Silesia, Poland) in the static composting open-air pile (located at: latitude 50° 18’ 30,71” N and longitude 18° 48’ 18,52” E) in a KNEER container system, as described by Musiol et al., 2011. In the composting pile, samples were incubated for 21 days at an average temperature of 61 ºC (± 5 ºC) with an average pH of 6.9. The samples were run in triplicate and the experiments were conducted between September and October 2015. In the
container system, the samples were incubated for 21 days in three cages at an average temperature of 60 °C (± 5 °C) with an average pH of 7.5. The cages with the materials studied were placed into composting systems at a depth of 1 meter below the compost surface.

2.2.2. Abiotic degradation test under the laboratory conditions

The samples were incubated in distilled water at 70 °C over a period of 70 days, according to norm ISO (International Standard: ISO 15814). The samples were inserted into 30-mL screw-capped vials, containing 25 mL of medium, and then placed in a laboratory oven at 70 °C. The samples were each run in triplicate. After a specified time of incubation the samples were removed from the vials and cleaned by washing in distilled water, they were then drained on blotting paper and then dried to a constant mass under a vacuum at 25 °C.

2.3. Measurements

2.3.1. Gel Permeation Chromatography (GPC) analysis

The GPC experiments for the PLA/PBAT samples were conducted as described previously by Sikorska et al. (2015).

2.3.2. $^1$H nuclear magnetic resonance (NMR) spectroscopy

$^1$H NMR spectra were recorded using a Bruker-Advance spectrometer as described by Rydz et al., (2015b). The blend composition was determined based on the integration of protons from the methine group of the PLA component (at $\delta = 5.20$ ppm) and protons of the methylene group in the aromatic and aliphatic dyads of the PBAT component (region between $\delta = 4.0$ to 4.5 ppm) (Rychter et al., 2010).

2.3.3. pH measurement

The pH measurements of the compost according to norm (PN-Z-15011-3:2001) were carried out as described previously by Sikorska et al. (2015).

2.3.4. Imaging of sample surfaces

Macroscopic changes in the surface of the materials tested were visualized using a digital camera (Olympus E-410), while microscopic changes were analyzed using an optical microscope and a scanning electron microscope (SEM). Optical 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 100x. SEM/EDS studies were performed using a Quanta 250 FEG (FEI Company, USA) high resolution environmental SEM operated at 10 kV acceleration voltages. The samples were observed without a coating, under low vacuum (80 Pa) conditions using a backscattered electron (BSE) detector. Energy dispersive X-ray spectroscopy (EDS) was used for analysis of elemental composition. The spectra were collected by an EDAX Apollo SDD spectrometer with Genesis V6.20 software.

2.3.5. Thermal properties
Thermal analysis was carried out on a Mettler-Toledo TGA/DSC STARe System, from 25 to 800 °C at a heating rate of 10 °C/min, under a constant flow of 60 mL/min of nitrogen. The obtained TGA data were analyzed using the Mettler-Toledo Star System SW 9.30.
Thermal characteristics of the materials studied were also obtained using a TA DSC 2010 apparatus (TA Instruments, New Castle, DE). The first calorimetric trace (I-scan, preliminary heating run) in which the thermal history was suppressed, were acquired from -80 °C to 200 °C at a heating rate of 20 °C/min, under a nitrogen atmosphere (flow rate = 50 mL/min). The instrument was calibrated with indium and gallium standards. The melting temperature ($T_m$) was taken as the peak maximum of the melting endotherm.

2.3.6. Measurement of the contact angle
Contact angle measurements (Q) for the tested material’s surface properties were measured statically using a contact angle goniometer CAM101 (KSV Instruments). The water contact angles were determined in air using the sessile-drop method. A series of images for the water drops (3 µL) were acquired during 15 s, and the average contact angle value was calculated. The contact angle measurements were performed on dry surfaces at 20 °C. An average of five values of contact angles from different parts of the samples was calculated. Two samples of each surface were used for measurements.

3. Results and Discussion
(Bio)degradation studies were conducted for prototype products made by the Bioerg Company, Poland. The changes of the surface and the changes of the average molar mass of samples (determined by GPC) are indicators of the degradation progress. The thermal characteristics of the materials during the degradation process were determined by TGA and DSC results. These outcomes led to important findings about the changes in the thermal
properties, crystallinity and thermal stability. The SEM studies enabled the identification of the additives in the samples based on chemical composition (Bart JCJ, 2006).

Macro- and microscopic visual evaluation of the samples during the degradation process indicated erosion as well as tarnishing of the film’s surface beginning from the 21st day of incubation in both composting systems. This observation is easy to see especially in the microscopic images shown in Fig 1. After 21 days of degradation the deterioration of the investigated films, F/17 and F/40 samples in the composting pile and containers began to crack. Disintegration of the film samples also began after 21 days of the reference abiotic degradation tests. Both films with 17 and 40 % of PLA in their blends during degradation showed similar morphological changes that occurred predominately on the sample surface. The thicker T/40 samples showed little change for 21 days, only the discoloration of samples that were placed in direct contact with compost was noticed (Fig. 1).

**Fig. 1.** Selected macro- (A) and microscopic (B) images of samples before (0) and after 21 days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.

The observed changes of the samples incubated in water and both composting systems: pile and containers, confirmed the fastest deterioration of thin films was with 17 % content of PLA in the blend (F/17) while the slowest were the second film that contained 40 % content of PLA in the blend (F/40) and the thickest sample of the final product with the same content of PLA (T/40).

The SEM micrographs of all investigated samples indicated the presence of white inclusions in the polymeric matrix (Fig. 2). The energy-dispersive spectroscope (EDS) scan analysis of selected regions showed the presence of Mg and Si which has most likely originated from a commercial additive, hydrated magnesium silicate $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (talc). Talc powder is often used as a dye and a filler, also used in the food industry (food additive number E553b) (Whaling et al. 2006, Commission delegated regulation (eu) no 1363/2013).

**Fig. 2.** Selected scanning electron microscopy with microanalysis (SEM-EDS) micrograph of plain T/40 sample surface at a magnification of 2500x.

Talc shows the dichotomy of wetting properties independent of relative humidity (RH). At low RH water adsorbs readily on the surface of talc because adhesive interactions in talc are
strong enough. However, at saturation the water-water interactions (cohesion) overcome talc adhesion and thus water beads up on its surface (Rotenberg et al. 2011). The comparison of average contact angle values (78.74, 83.79 and 96.14 for F/17, F/40 and T/40 respectively) confirmed that the T/40 surface was the most hydrophobic with the highest contact angle value and the most stable of the drops during the longer contact with the examined surfaces. On the contrary, in the case of F/17 and F/40 samples, a drop of water left on the surface for the same time (longer than the measurement time) reduced the contact angle value by up to several degrees and it was probably caused by the influence of talc. Thus, the presence of talc in all of the samples may have disturbed their behavior towards water and consequently altered the degradation profile.

The reliable monitoring of the sample’s mass changes during the degradation process under industrial composting conditions was impossible. Thus Fig. 3 presents the only mass changes of materials that occurred during the incubation in distilled water at 70 °C.

**Fig. 3.** The mass changes of materials studied during the abiotic degradation testing at 70 °C.

Systematic remaining mass decrease was found in all of the studied samples. At the beginning of degradation, the mass of blends decreased slightly with a more noticeable molar mass loss (Fig. 3 and Fig. 4), which is typical for the hydrolytic degradation mechanism (Rydz et al., 2013). It is well known that the degradation of PLA in an aqueous environment occurs through the hydrolysis of ester bonds, which increases the amount of carboxy end-groups (-COOH) and generates the autocatalytic effect (Espartero et al. 1996). At the initial stage, the biggest mass loss was observed for thin film samples with a higher content of the PLA component in the blend, F/40. The mass loss for the thicker sample, with 40 % PLA, (T/40) began later but at the end of the degradation it reached the highest volume. It is important to notice that PLA shows lower absorption of water in blends than the second component PBAT (Osman et al. 2014, Willett et al. 2002). Also and the presence of the talc in all the samples could have had an influence on water absorption. The TG analysis shows that the amount of residue is 7, 8 and 15 % for F/17, F/40 and T/40 samples, respectively. This implies a higher quantity of talc in the T/40 sample. Additionally, at the beginning of the incubation for thick T/40 samples the degradation products could be closed inside the polymeric matrix which is consistent with the mechanism of autocatalytic hydrolysis proposed by Vert (Espartero et al. 1996).
The degradation process in all environments resulted in a decrease of the average molar mass of the investigated samples but at a different rate (Fig. 4).

**Fig. 4.** The changes in molar mass of the investigated samples before degradation (0) and after 21 days of incubation in: C - container, H - distilled water at 70 °C.

After 21 days of incubation (Fig. 4) the comparable shifting of the monomodal traces to the higher retention volume values was observed for all of the investigated samples. However, this phenomenon was more visible for the thicker T/40 sample after incubation in distilled water, which may suggest that the autocatalytic effect of the hydrolytic degradation for this sample occurred (Espartero et al. 1996). What was also evidenced by an increase in the molar-mass dispersity was the higher presence of populations which degraded at different rates from the surface/interior parts.

On the basis of ¹H NMR spectra the PLA/PBAT composition changes appearance during the degradation in all environments, after 21 days incubation, they were calculated and are presented in Table 2 (Rychter et al., 2010).

**Table 2.** The changes of PLA content (mol%) of samples incubated for 21 days in different environmental conditions, calculated from ¹H NMR spectra.

Slight changes in the blend composition were observed from the beginning of the incubation in distilled water. This suggests that the degradation of both components in all of the materials studied under these conditions occurs at almost the same rate until the 21st day of the degradation test, and only after that, the largest difference started to appear. The total reduction of the PLA component of the thin sample (F/17) was observed after 42 days of the abiotic degradation test under the conditions given and for the thicker sample (T/40), after 70 days of the process. This phenomenon is not observed for the thin film sample F/40 with the same amount of PLA, in which the 15 mol% of PLA after 70 days of degradation in distilled water is still present (Yang et al. 2005). This result also confirms the contribution of the autocatalytic effect during the hydrolytic degradation in distilled water occurring in the T/40
sample. For the F/17 sample, the decrease of PLA content under composting conditions is higher than during the degradation in distilled water at 70 °C after the same time period (see Table 2). Rychter et al. (2010) showed that the mechanism of PBAT degradation in the standardized, sandy soil proceeds enzymatically. This may suggest that under industrial composting conditions this mechanism for PBAT as the blend component may have an impact on the degradation process. In the container system, the more favorable conditions for enzymatic degradation exists, thus leaching of PLA degradation products from the blend is facilitated by the degradation of PBAT. Moreover, Oyama et al. (2011) indicated that the products of PLA degradation catalyzes the hydrolytic degradation of the PBAT component in the blend. This conclusion points out that for the blend with a lower content of PLA, a lower hydrolytic degradation rate of PBAT is observed and it results in a lower decrease of $M_n$ during incubation in a container (see Fig. 4). In the case of materials with higher PLA content such as F/40 and T/40 samples, the observed higher $M_n$ changes suggests hydrolytic degradation of both blend components. The obtained results and the compositional changes suggest the enzymatic degradation of both components under composting conditions. Thus, in the case of the F/17 sample, the enzymatic degradation of PBAT, especially in the container, may play an important role. Moreover, the changes of the blend composition observed during the degradation process under industrial composting conditions suggests that the degradation of the blend components are more rapid in the container system than in composting pile. This is probably caused by the higher humidity level of the compost in the container system. The static composting pile with natural aeration, located in the open area, is exposed to all weather conditions, which can affect the composting process. In opposition to this, the composting process in the closed system is independent of weather conditions and it allows for better control of the process than in open systems (Kale et al., 2007a).

The behavior of the investigated materials during the degradation process in different environments was characterized using thermogravimetric analysis. The first differential TGA curve (DTG thermograms) obtained for the materials after 21 days of incubation are plotted in Fig. 5.

Fig. 5. First differential TGA curve of investigated materials before (0) and after 21 days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.
The thermal effects of both components in the investigated blend samples are similar to each other. This may suggest that these effects partially overlap, which is more visible in the samples with higher PLA content. After degradation in all environments, for the thicker sample (T/40) in the part of the curve in the low temperature region, which corresponds to the PLA, a broader DTG peak than for F/40 was observed. This result confirms the participation of the autocatalytic effect in the T/40 sample’s degradation process (Espartero et al. 1996). After the degradation of all the investigated samples in the container system had occurred, the changes in the DTG peak, which corresponds to the PBAT component, was also observed. This indicated that the conclusions, based on the changes in the composition and molar masses of the enzymatic mechanism of PBAT degradation under these conditions are correct with minor contributions of hydrolytic degradation of the investigated material, depending on the PLA content and/or the presence of talc in the samples (Rychter et al., 2010).

The DSC results presented in Fig. 6 suggest that the samples studied are not compatible. All the DSC thermograms showed two broad peaks with the maximum value corresponding to both PLA and PBAT component’s melting temperatures.

**Fig. 6.** DSC plot of the investigated materials before (0) and after 21 days of incubation in: CP - composting pile, C - container, H - distilled water at 70 °C.

It is apparent from the DSC traces of the F/40 and T/40 samples after degradation under industrial composting conditions that the melting peak, which corresponds to PLA, is well defined. This result suggests that after degradation in these conditions, more crystalline solid domains with regular crystals were obtained, which in turn results in a sharper melting peak, meaning (the material goes from solid to liquid in a very short temperature range) (Lucas et. all 2008). After degradation in distilled water at 70 °C the PLA melting peak is more expanded. The observed changes in this region for all of the samples could result from the presence of the shorter polymer chains formed via the hydrolysis of ester bonds and/or the formation of small crystals with irregular structures existing in rigid amorphous domains (Iannace et al. 2001). For the F/17 sample after degradation in the container system, this phenomenon is also observed. This may suggest that under these conditions the regular crystals cannot be properly formed because of the faster leaching of low molar mass PLA oligomers to the degradation medium, which could be facilitated by the degradation of PBAT, as was described above.
4. Conclusion

The obtained results indicate that both components of the blend are degraded, but at different rates. The differences in the degradation rate of the materials tested, with a similar content of the PLA component, could be caused by differences in their thickness and/or the presence of commercial additives used during the processing stage. The use of a larger quantity of talc in the production of disposable bags may cause differences in the water absorption of polymeric materials depending on the degradation environment humidity. Additionally, in the case of the sample of thin film with a lower content of PLA (17 mol%), besides hydrolysis, enzymatic degradation in the container system probably occurred. Therefore, in order to precisely determine the performance parameters of final products, all factors need be considered, because even if we use materials of the same composition, but with differences in their thickness or thermal and processing history, they may not behave in the same way during usage.

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Author Contributions

This manuscript was written through contributions from all authors. Marta Musiol contributed 80 %, Wanda Sikorska contributed 15 %, while other authors within 5 % contributed equally to this work. All authors have given approval to the final version of the manuscript.
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Polymers 9(7), 257.


**Table 1.** Plain materials studied – prototype products of Bioerg Company, Poland

<table>
<thead>
<tr>
<th>Product type</th>
<th>Sample name</th>
<th>PLA content [mol%]</th>
<th>Thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>F/17</td>
<td>17±0.5</td>
<td>0.02±0.01</td>
</tr>
<tr>
<td></td>
<td>F/40</td>
<td>40±1.0</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>Disposable bag market</td>
<td>T/40</td>
<td>40±0.5</td>
<td>0.10±0.01</td>
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</tbody>
</table>
**Table 2.** The changes of PLA content (mol%) of samples incubated for 21 days in different environmental conditions, calculated from $^1$H NMR spectra.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Degradation environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
</tr>
<tr>
<td>F/17</td>
<td>14±1.0</td>
</tr>
<tr>
<td>F/40</td>
<td>34±0.5</td>
</tr>
<tr>
<td>T/40</td>
<td>35±1.0</td>
</tr>
</tbody>
</table>
Figure 1
Click here to download high resolution image
Figure 3

The graph shows the remaining mass (%) over time (days) for different conditions labeled as F/17, F/40, and T/40. The data points are plotted with error bars, indicating variability in the measurements. The mass decreases exponentially over time, with F/17 showing a slightly steeper decrease compared to F/40 and T/40.
Figure 6

Click here to download high resolution image