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

Corresponding Author: Dr. Marta Musiol,

Corresponding Author's Institution: Polish Academy of Sciences

First Author: Marta Musiol

Order of Authors: Marta Musiol; Wanda Sikorska; Henryk Janeczek; Wojciech Wałach; Anna Hercog; Brian Johnston; Joanna Rydz

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.

Cover Letter

Zabrze, 12.04.2018

Marta Musioł

Centre of Polymer and Carbon Materials

ul. Marii Curie-Sklodowskiej 34

41-819 Zabrze

POLAND

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

Reviewer #4 Comment	Author' Response	Revised Text
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.	Highlights were corrected	Revised manuscript
2. Line 28, Abstract: "Therefore" in this sentence is not correctly used.	Abstract was reworded and corrected	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
3. The standard deviation was not contained in the data shown in Tables 1 & 2.	Tables 1 and 2 were corrected	Page 4 Line 115 and page 9 Line 281 in new submission
4. Line 49: Delete "being" 5. Line 50: Change both "were"s to "are"	Corrected	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
6. Lines 83-85: The sentence is not correct.	Corrected	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
7 Lines 276-277: "which may suggest that the autocatalytic effect of the hydrolytic degradation for this sample occurred." Do you have any reference to support this explanation?	Corrected	…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

(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

Marta Musioł[a]*****, Wanda Sikorska[a], Henryk Janeczek[a], Wojciech Wałach[a], Anna Hercog[a], Brian Johnston[b], Joanna Rydz[a]

[a] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34. M. Curie-Skłodowska St., 41-819 Zabrze, Poland

[b] University of Wolverhampton, Faculty of Science and Engineering, Department of Biology, Chemistry and Forensic Science, Wulfruna Street, Wolverhampton, WV1 1SB, UK

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.

Corresponding author. E-mail: m.musiol@cmpw-pan.edu.pl; Tel.: +48 32 271-60-77; Fax: +48 32 271-29-69

1   Marta Musioł[a]*****, Wanda Sikorska[a], Henryk Janeczek[a], Wojciech Wałach[a], Anna Hercog[a],

2   Brian Johnston[b], Joanna Rydz[a]

3   [a] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34. M. Curie-

4   Skłodowska St., 41-819 Zabrze, Poland

5   [b] University of Wolverhampton, Faculty of Science and Engineering, Department of Biology,

6   Chemistry and Forensic Science, Wulfruna Street, Wolverhampton, WV1 1SB, UK

7   *mmusiol@cmpw-pan.edu.pl

8

9   **(BIO)DEGRADABLE POLYMERIC MATERIALS FOR A SUSTAINABLE FUTURE-**

10   **PART 1. ORGANIC RECYCLING OF PLA/PBAT BLENDS IN THE FORM OF**

11   **PROTOTYPE PACKAGES WITH LONG SHELF-LIFE**

12

13   **Abstract**

14   Prediction studies of advanced (bio)degradable polymeric materials are crucial when their

15   potential applications as compostable products with long shelf-life is considered for today's

16   market. The aim of this study was to determine the effect of the polylactide (PLA) content in

17   the blends of PLA and poly(butylene adipate-*co*-terephthalate) (PBAT); specifically how the

18   material's thickness corresponded to changes that occurred in products during the degradation

19   process. Additionally, the influence of talc on the degradation profile of all samples in all

20   environments was investigated. It was found that, differences in the degradation rate of

21   materials tested with a similar content of the PLA component could be caused by differences

22   in their thickness, the presence of commercial additives used during processing or a

23   combination of both. The obtained results indicated that the presence of talc may interfere

24   with materials behaviour towards water and consequently alter their degradation profile.

25

26   **Keywords**: organic recycling, biodegradation, hydrolytic degradation, packages,

27   poly(butylene adipate-*co*-terephthalate), polylactide, talc

28

29   **1. Introduction**

30

31   The key to achieving success and increased presence in the bioeconomy industry is to

32   understand both the advantages and limitations of biodegradable and biobased products.

33   Biodegradable polymers are now the material of choice due to the plastics industry needing to

34   change their strategy as a result of years of pollution. This influence has become the steady

35 driving force behind the manufacturing sector in Europe over the last few years (Rydz et al.,

36 2018). Conventional polymers available today are thought to have many advantages, such as

37 good processability, hydrophobicity and having excellent barrier properties. However, these

38 materials are characterised by high resistance to biological agents and the widespread use of

39 them for packaging has made them the cause of an array of environmental problems. Plastic

40 waste deposited in landfills occupies more new areas of ground each year and even threatens

41 our oceans. One of the ways to solve this growing problem is to introduce and promote the

42 consistent usage of packaging made from natural or biodegradable polymers into the market

43 (Ghanbarzadeh and Almasi, 2013; Sam et al., 2016; Narodoslawsky et al., 2015).

44 Biodegradable packages with special marks or indicators could be separated from the

45 municipal waste stream and directed into organic recycling. This could be achieved by

46 collecting them together with the organic waste arising from households (Höglund et al.,

47 2012; Kale et al., 2006, 2007a; Musioł et al., 2015; Sikorska et al., 2008, 2012; Swift, 2015).

48 According to PlasticsEurope and European Bioplastics (nova-Institute) the amount of global

49 plastic production in 2017 was estimated at 340 million tonnes; of this amount 2.05 million

50 tonnes are biobased plastics and 880 000 tonnes are biobased biodegradable polymers (Report

51 European Bioplastics, 2017). Therefore, it is extremely important to increase consumer

52 awareness about biodegradable polymeric materials and introduce them to the market, so

53 biodegradable packaging will become an integral part of their lives. The global introduction

54 of biodegradable polymeric materials for packaging must be preceded by a number of

55 changes, such as the development of new technology, the improvement of the infrastructure

56 of composting, as well as the financial capacity and the appropriate policies that are required

57 (DSTI/STP/BIO(2013)6/FINAL, 2013; Shahzad et al., 2017; Narodoslawsky, 2010; Koller et

58 al., 2017). Thus, research, especially proof of concept studies, in this area are still required.

59 The value chain of biodegradable polymeric materials comes from the production of polymers

60 through to the consumer and then through waste management (PLASTICE project) and

61 research should be carried out at every link of this chain.

62 The term biodegradable is used to describe those materials, which are degraded by the

63 enzymatic action of microorganisms (bacteria and fungi). Biodegradation can occur under

64 aerobic and anaerobic conditions. The final degradation products of the process under aerobic

65 conditions are CO_2, H_2O and biomass (Adamus et al., 2006; Sikorska et al., 2015). The

66 literature reviewed indicates that aliphatic polyesters are now considered potential

67 biomaterials for applications in agriculture, medicine, pharmacy and packaging (Rydz et al.,

68 2015a; Sikorska et al., 2014; Musioł et al., 2016a, 2016b). PLA exhibits a high tensile

69   modulus, resistance to UV radiation and fats, and the ability to be processed by conventional

70   methods (Ahmed and Varshney, 2011; Ingaro et al., 2015; Jabeen et al., 2015; Kale et al.,

71   2007b, Jost and Kopitzky, 2015). However, there are several examples where PLA-based

72   materials did not meet the requirements as a packaging material, especially for long shelf-life

73   products (Rydz et al., 2013a, 2013b, 2015b). Aliphatic-aromatic copolyesters can be applied

74   in package production due to the good functionality of their aromatic polyesters and the

75   biodegradability of aliphatic polyesters (Witt et al., 2001; Rychter 2006, 2010, 2011;

76   Żenkiewicz et al., 2013).PBAT is a linear statistical aliphatic-aromatic copolyester consisting

77   of 1,4-butanediol and terephthalic acid monomers as rigid units and 1,4-butanediol and adipic

78   acid monomers as flexible units. PBAT with the content of terephthalic acid higher than 35

79   mol% has better mechanical and thermal properties (Siyamak et al., 2012; Bohlmann, 2005).

80   However, the increase of its content is followed by a significant decrease in the

81   biodegradation rate as the growing amount of aromatic units elevates resistance against

82   microorganisms (Vroman and Tighzert, 2009; Kijchavengkul et al., 2010). On the market,

83   BASF (Ecoflex®) and Novamont (Origo-Bi[TM], former Eastar-Bio[TM]/Eastman with 30-70 %

84   renewable content) PBAT producers are widely known (Jiang and Loos, 2016; News/Press

85   releases, 2013a, 2013b). Additionally, PBAT is processable on conventional blow film plants

86   applied for low-density polyethylene what can contribute to the reduction of the cost of

87   producing the material (Plasticsportal.net). The PBAT copolyester is used commercially in

88   food packaging, as an agricultural plastic and it is also used in sporting goods. Recent studies

89   have shown that the aliphatic-aromatic copolyester and polylactide commercial blend

90   demonstrates good stability during aging in cosmetic simulants, which is important for

91   prospective applications of this polymeric material as compostable packing for products with

92   a long shelf-life (Sikorska et al., 2017).

93

94   **2. Materials and Methods**

95   This paper presents a (bio)degradation study of PLA and PBAT blends in the form of

96   prototype packages with long shelf-life. The biodegradation tests were performed under

97   industrial composting conditions in a pile and in a container system. Additionally, an abiotic

98   degradation test was carried out under laboratory conditions. The selected materials allowed

99   the determination of the effect of PLA content (17 and 40 mol%) in the films on their

100   degradation process and a comparison of the degradation of materials with different thickness

101   and the same molar content (40 mol%) of PLA. The changes of molar mass, molar-mass

102   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 ℃ 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 Musioł et al., 2011. In the composting pile, samples were incubated for 21 days at an average temperature of 61 ℃ ($\pm$ 5 ℃) 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 ℃ ($\pm$ 5 ℃) 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.

137 *2.2.2. Abiotic degradation test under the laboratory conditions*

138 The samples were incubated in distilled water at 70 ºC over a period of 70 days, according to

139 norm ISO (International Standard: ISO 15814). The samples were inserted into 30-mL screw-

140 capped vials, containing 25 mL of medium, and then placed in a laboratory oven at 70 ºC. The

141 samples were each run in triplicate. After a specified time of incubation the samples were

142 removed from the vials and cleaned by washing in distilled water, they were then drained on

143 blotting paper and then dried to a constant mass under a vacuum at 25 ºC.

144

145 *2.3. Measurements*

146

147 *2.3.1. Gel Permeation Chromatography (GPC) analysis*

148 The GPC experiments for the PLA/PBAT samples were conducted as described previously by

149 Sikorska et al. (2015).

150

151 *2.3.2. ^{1}H nuclear magnetic resonance (NMR) spectroscopy*

152 ^{1}H NMR spectra were recorded using a Bruker-Advance spectrometer as described by Rydz

153 et al., (2015b). The blend composition was determined based on the integration of protons

154 from the methine group of the PLA component (at $\delta = 5.20$ ppm) and protons of the

155 methylene group in the aromatic and aliphatic dyads of the PBAT component (region

156 between $\delta = 4.0$ to 4.5 ppm) (Rychter et al., 2010).

157

158 *2.3.3. pH measurement*

159 The pH measurements of the compost according to norm (PN-Z-15011-3:2001) were carried

160 out as described previously by Sikorska et al. (2015).

161

162 *2.3.4. Imaging of sample surfaces*

163 Macroscopic changes in the surface of the materials tested were visualised using a digital

164 camera (Olympus E-410), while microscopic changes were analysed using an optical

165 microscope and a scanning electron microscope (SEM). Optical analysis was performed using

166 a Zeiss polarizing microscope (Opton-Axioplan) equipped with a Nikon Coolpix 4500 colour

167 digital camera. Pictures were taken at a magnification of 100x. SEM/EDS studies were

168 performed using of a Quanta 250 FEG (FEI Company, USA) high resolution environmental

169 SEM operated at 10 kV acceleration voltages. The samples were observed without a coating,

170 under low vacuum (80 Pa) conditions using a backscattered electron (BSE) detector. Energy

171 dispersive X-ray spectroscopy (EDS) was used for analysis of elemental composition. The

172 spectra were collected by an EDAX Apollo SDD spectrometer with Genesis V6.20 software.

173

174 *2.3.5. Thermal properties*

175 Thermal analysis was carried out on a Mettler-Toledo TGA/DSC STARe System, from 25 to

176 800 °C at a heating rate of 10 °C/min, under a constant flow of 60 mL/min of nitrogen. The

177 obtained TGA data were analysed using the Mettler-Toledo Star System SW 9.30.

178 Thermal characteristics of the materials studied were also obtained using a TA DSC 2010

179 apparatus (TA Instruments, New Castle, DE). The first calorimetric trace (I-scan, preliminary

180 heating run) in which the thermal history was suppressed, were acquired from -80 °C to 200

181 °C at a heating rate of 20 °C/min, under a nitrogen atmosphere (flow rate = 50 mL/min). The

182 instrument was calibrated with indium and gallium standards. The melting temperature (T_m)

183 was taken as the peak maximum of the melting endotherm.

184

185 *2.3.6. Measurement of the contact angle*

186 Contact angle measurements (Q) for the tested material's surface properties were measured

187 statically using a contact angle goniometer CAM101 (KSV Instruments). The water contact

188 angles were determined in air using the sessile-drop method. A series of images for the water

189 drops (3 µL) were acquired during 15 s, and the average contact angle value was calculated.

190 The contact angle measurements were performed on dry surfaces at 20 °C. An average of five

191 values of contact angles from different parts of the samples was calculated. Two samples of

192 each surface were used for measurements.

193

194 **3. Results and Discussion**

195

196 (Bio)degradation studies were conducted for prototype products made by the Bioerg

197 Company, Poland. The changes of the surface and the changes of the average molar mass of

198 samples (determined by GPC) are indicators of the degradation progress. The thermal

199 characteristics of the materials during the degradation process were determined by TGA and

200 DSC results. These outcomes led to important findings about the changes in the thermal

201 properties, crystallinity and thermal stability. The SEM studies enabled the identification of

202 the additives in the samples based on chemical composition (Bart JCJ, 2006).

203 Macro- and microscopic visual evaluation of the samples during the degradation process

204 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 $Mg_3Si_4O_{10}(OH)_2$ (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

238   value and the most stable of the drops during the longer contact with the examined surfaces.

239   On the contrary, in the case of F/17 and F/40 samples, a drop of water left on the surface for

240   the same time (longer than the measurement time) reduced the contact angle value by up to

241   several degrees and it was probably caused by the influence of talc. Thus, the presence of talc

242   in all of the samples may have disturbed their behavior towards water and consequently

243   altered the degradation profile.

244   The reliable monitoring of the sample's mass changes during the degradation process under

245   industrial composting conditions was impossible. Thus Fig. 3 presents the only mass changes

246   of materials that occurred during the incubation in distilled water at 70 °C.

247

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

249

250   Systematic remaining mass decrease was found in all of the studied samples. At the beginning

251   of degradation, the mass of blends decreased slightly with a more noticeable molar mass loss

252   (Fig. 3 and Fig. 4), which is typical for the hydrolytic degradation mechanism (Rydz et al.,

253   2013). It is well known that the degradation of PLA in an aqueous environment occurs

254   through the hydrolysis of ester bonds, which increases the amount of carboxy end-groups (-

255   COOH) and generates the autocatalytic effect (Espartero et al. 1996). At the initial stage, the

256   biggest mass loss was observed for thin film samples with a higher content of the PLA

257   component in the blend, F/40. The mass loss for the thicker sample, with 40 % PLA, (T/40)

258   began later but at the end of the degradation it reached the highest volume. It is important to

259   notice that PLA shows lower absorption of water in blends than the second component PBAT

260   (Osman et al. 2014, Willett et al. 2002) and the presence of talc in all of the samples could

261   had an influence on water absorption. The TG analysis shows that the amount of residue is 7,

262   8 and 15 % for F/17, F/40 and T/40 samples, respectively. This implies a higher quantity of

263   talc in the T/40 sample. Additionally, at the beginning of the incubation for thick T/40

264   samples the degradation products could be closed inside the polymeric matrix which is

265   consistent with the mechanism of autocatalytic hydrolysis proposed by Vert (Espartero et al.

266   1996).

267   The degradation process in all environments resulted in a decrease of the average molar mass

268   of the investigated samples but at a different rate (Fig. 4).

269

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

303 facilitated by the degradation of PBAT. Moreover, Oyama et al. (2011) indicated that the
304 products of PLA degradation catalyzes the hydrolytic degradation of the PBAT component in
305 the blend. This conclusion points out that for the blend with a lower content of PLA, a lower
306 hydrolytic degradation rate of PBAT is observed and it results in a lower decrease of M_n
307 during incubation in a container (see Fig. 4). In the case of materials with higher PLA content
308 such as F/40 and T/40 samples, the observed higher M_n changes suggests hydrolytic
309 degradation of both blend components. The obtained results and the composition changes
310 suggest the hydrolytic degradation of both components under composting conditions. Thus, in
311 the case of the F/17 sample, the enzymatic degradation of PBAT, especially in the container,
312 may play an important role. Moreover, the changes of the blend composition observed during
313 the degradation process under industrial composting conditions suggests that the degradation
314 of the blend components are more rapid in the container system than in composting pile. This
315 is probably caused by the higher humidity level of the compost in the container system. The
316 static composting pile with natural aeration, located in the open area, is exposed to all weather
317 conditions, which can affect the composting process. In opposition to this, the composting
318 process in the closed system is independent of weather conditions and it allows for better
319 control of the process than in open systems (Kale et al., 2007a).
320 The behavior of the investigated materials during the degradation process in different
321 environments was characterised using thermogravimetric analysis. The first differential TGA
322 curve (DTG thermograms) obtained for the materials after 21 days of incubation are plotted in
323 Fig. 5.

324

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

327

328 The thermal effects of both components in the investigated blend samples are similar to each
329 other. This may suggest that these effects partially overlap, which is more visible in the
330 samples with higher PLA content. After degradation in all environments for the thicker
331 sample (T/40) in the part of the curve in the low temperature region, which corresponds to the
332 PLA, a broader DTG peak than for F/40 was observed. This result confirms the participation
333 of the autocatalytic effect in the T/40 sample's degradation process (Espartero et al. 1996).
334 After the degradation of all the investigated samples in the container systemthe changes in the
335 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. 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

370 sample of thin film with a lower content of PLA (17 mol%), besides hydrolysis, enzymatic

371 degradation in the container system probably occurred. Therefore, in order to precisely

372 determine the performance parameters of final products, all factors need be considered,

373 because even if we use materials of the same composition, but with differences in their

374 thickness or thermal and processing history, they may not behave in the same way during

375 usage.

376

387

388 **Author Contributions**

389 This manuscript was written through contributions from all authors. Marta Musioł contributed

390 80 %, Wanda Sikorska contributed 15 %, while other authors within 5 % contributed equally

391 to this work. All authors have given approval to the final version of the manuscript.

Literature

Adamus, G., Dacko, P., Musioł, M., Sikorska, W., Sobota, M., Biczak, R., Herman, B., Rychter, P., Krasowska, K., Rutkowska, M., Kowalczuk, M., 2006. Degradation of selected synthetic polyesters in natural conditions. Polimery 51, 539-546 (in Polish).

Ahmed, J., Varshney, S., 2011. Polylactides - chemistry, properties and green packaging technology: a review. Int. J. Food Prop. 14(1), 37-58.

Bart, J.C.J., 2006. Polymer additive analytics. Industrial practice and case studies. Firenze University Press.

Bohlmann, G.M., 2005. General characteristics, processability, industrial applications and market evolution of biodegradable polymers, in: Bastioli, C. (Ed.), Handbook of biodegradable polymers. Rapra, Shawbury, pp. 183-217.

Commission delegated regulation (eu) no 1363/2013. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013R1363&from=PL (accessed 28 September 2013).

Espartero, J.L., Rashkov, I., Li, S.M., Manolova, N., Vert, M., 1996. NMR analysis of low molecular weight poly(lactic acid)s. Macromolecules 29, 3535-3539.

Ghanbarzadeh, B., Almasi, H., 2013. Biodegradable polymers, in: Chamy, R., Rosenkranz, F. (Eds.), Biodegradation - Life of science. InTech, Rijeka, pp. 141-185.

Höglund, A., Odelius, K., Albertsson, A-C., 2012. Crucial differences in the hydrolytic degradation between industrial polylactide and laboratory-scale poly(L-lactide). ACS Appl. Mater. Interfaces 4, 2788-2793.

Iannace, S., Maffezzoli, A., Leo, G., Nicolais, L., 2001. Influence of crystal and amorphous phase morphology on hydrolytic degradation of PLLA subjected to different processing conditions. Polymer 42(8), 3799-3807.

Ingrao, C., Tricase, C., Cholewa-Wójcik, A., Kawecka, A., Rana, R., Siracusa, V., 2015. Polylactic acid trays for fresh-food packaging: A Carbon Footprint assessment. Sci. Total Environ. 537, 385-398.

International Standard: ISO 15814. Implants for surgery - copolymers and blends based on polylactide - in vitro degradation testing. International Organization for Standardization, Switzerland, 1999.

Jabeen, N., Majid, I., Nayik, G.A., 2015. Drying kinetics of potato using a self-designed cabinet dryer. Cogent Food Agric. 1(1), 6 pages.

Jiang, Y., Loos, K., 2016. Enzymatic synthesis of biobased polyesters and polyamides. Polymers 8(7), 243.

Jost, V., Kopitzky, R. 2015. Blending of polyhydroxybutyrate-co-valerate with polylactic acid for packaging applications-reflections on miscibility and effects on the mechanical and barrier properties. Chem. Biochem. Eng. Q., 29(2), 221-246.

Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S., Singh, P.S., 2007a. Compostability of bioplastic packaging materials: an overview. Macromol. Biosci. 7(3), 255-277.

Kale, G., Auras, R., Singh, S., Narayan, R., 2007b. Biodegradability of polylactide bottles in real and simulated composting conditions. Polym. Test. 26, 1049-1061.

Kale, G., Auras, R., Singh, S., 2006. Degradation of commercial biodegradable packages under real composting and ambient exposure conditions. J. Polym. Environ. 14, 317-334.

Kijchavengkul, T., Auras, R., Rubino, M., Alvarado, E., Camacho Montero, J.R., Rosales, J.M., 2010. Atmospheric and soil degradation of aliphatic - aromatic polyester films. Polym. Degrad. Stab. 95, 99-107.

Koller, M., Maršálek, L., de Sousa Dias, M. M., Braunegg, G., 2017. Producing microbial polyhydroxyalkanoate (PHA) biopolyesters in a sustainable manner. N. Biotechnol., 37, 24-38.

Lucas, N., Bienaime, C., Belloy, C., Queneudec, M., Silvestre, F., Nava-Saucedo, J-E., 2008. Polymer biodegradation: mechanisms and estimation techniques. - A review. Chemosphere 73(4), 429-442.

445   Musioł, M., Sikorska, W., Adamus, G., Kowalczuk, M., 2016a. Forensic engineering of
446   advanced polymeric materials. Part III - Biodegradation of thermoformed rigid PLA
447   packaging under industrial composting conditions. Waste Manage. 2, 69-76.

448   Musioł, M., Sikorska, W., Kowalczuk, M., Adamus, G., 2016b. The development of
449   sustainable bioplastics for new applications in packaging industry. Int. J. Environ. Agric.
450   Res. 2(2), 117-124.

451   Musioł, M., Sikorska, W., Adamus, G., Janeczek, H., Kowalczuk, M., Rydz, J., 2015
452   (Bio)degradable polymers as a potential material for food packaging: studies on
453   the(bio)degradation process of PLA/(R,S)-PHB rigid foils under industrial composting
454   conditions. Eur. Food Res. Technol. 242, 815-823.

455   Musioł, M.T., Rydz, J., Sikorska, W.J., Rychter, P.R., Kowalczuk, M.M., 2011. A preliminary
456   study of the degradation of selected commercial packaging materials in compost and
457   aqueous environments. Pol. J. Chem. Tech. 13, 55-57.

458   Narodoslawsky, M., Shazad, K., Kollmann, R., Schnitzer, H., 2015. LCA of PHA production
459   - Identifying the ecological potential of bio-plastic. Chem. Biochem. Eng. Q. 29(2), 299-
460   305.

461   Narodoslawsky, M., 2010. Structural prospects and challenges for bio commodity processes.
462   Food Technol. Biotechnol. 48(3), 270-275.

463   News/Press releases. Compostable organic waste bags made of Ecovio[®] approved in
464   Ludwigshafen, Germany. http://www.plasticsportal.net/wa/plasticsEU/portal/show/
465   common/plasticsportal_news/2013/13_337 (accessed 20 June 2013).

466   News/Press releases. Novamont buys Eastman's 'Eastar Bio' technology.
467   http://www.icis.com/resources/news/2004/09/08/611549/novamont-buys-eastman-s-
468   eastarbio-technology/ (accessed 08 September 2013).

469   Organisation for Economic Co-operation and Development, 2013. Policies for bioplastics in
470   the context of a bioeconomy. DSTI/STP/BIO(2013)6/FINAL (published online: 24
471   September 2014).

472 Osman, M.J., Ibrahim, N.A., Sharif, J., WanYunus, W.M.Z., 2014. Study on water absorption
473   and biodegradation of polylactic acid/poly (butylene adipate-co-terephthalate)
474   nanocomposite. ChemXpress 5(2), 66-72.

475 Oyama HT, Tanaka Y, Hirai S, Shida S, Kadosaka A. Water-disintegrative and biodegradable
476   blends containing poly(L-lactic acid) and poly(butylene adipate-co-terephthalate). J
477   Polym Sci Part B Polym Phys 2011;49(5):342-354.

478 PLASTiCE project, http://www.plastice.org (accessed 10 October 2016).

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

482
483 PN-Z-15011-3:2001 Municipal solid waste compost - Determination of pH, content of
484   organic substance, organic carbon, nitrogen, phosphorus and potassium.

485 Report European Bioplastics, 2017. Bioplastics market data 2017, http://docs.european-
486   bioplastics.org/publications/market_data/2017/Report_Bioplastics_Market_Data_2017.p
487   df (accessed 30 January 2017)

488 Rotenberg, B., Patel, A.J., Chandler, D., 2011. Molecular explanation for why talc surfaces
489   can be both hydrophilic and hydrophobic. J. Am. Chem. Soc. 133, 20521-20527.

490 Rychter, P., Biczak, R., Herman, B., Zawierucha, I., Musioł, M., Sobota, M., Kowalczuk, M.,
491   2011. Environmental degradation of aromatic-aliphatic polyester blends. Evaluation of
492   degradation products in soil and their phytotoxicological impact. Polish J. Environ. Stud.
493   20, 293-298.

494 Rychter, P., Kawalec, M., Sobota, M., Kurcok, P., Kowalczuk, M., 2010. Study of aliphatic-
495   aromatic copolyester degradation in sandy soil and its ecotoxicological impact.
496   Biomacromolecules 11, 839-847.

497 Rychter, P, Biczak, R., Herman, B., Smyłła, A., Kurcok, P., Adamus, G., Kowalczuk, M.,
498   2006. Environmental degradation of polyester blends containing atactic poly(3-

499 hydroxybutyrate). Biodegradation in soil and ecotoxicological impact.
500 Biomacromolecules 7, 3125-3131.

501 Rydz, J., Musioł, M., Zawidlak-Węgrzyńska, B., Sikorska, W., 2018. Present and future of
502 (bio)degradable polymers for food packaging applications, in: Grumezescu, A.M.,
503 Holban, A.M. (Eds.), Handbook of food bioengineering. Elsevier, Romania, pp. 429-465.

504 Rydz, J., Sikorska, W., Kyulavska, M., Christova, D., 2015a. Polyester-based (bio)degradable
505 polymers as environmentally friendly materials for sustainable development. Int. J. Mol.
506 Sci. 16(1), 564-596.

507 Rydz, J., Wolna-Stypka, K., Adamus, G., Janeczek, H., Musioł, M., Sobota, M.,
508 Marcinkowski, A., Krzan, A., Kowalczuk, M., 2015b. Forensic engineering of advanced
509 polymeric materials. Part 1 - Degradation studies of polylactide blends with atactic
510 poly[(R,S)-3-hydroxybutyrate] in paraffin. Chem. Biochem. Eng. Q. 29(2), 247-259.

511 Rydz, J., Adamus, G., Wolna-Stypka, K., Marcinkowski, A., Misiurska-Marczak, M.,
512 Kowalczuk, M.M., 2013a. Degradation of polylactide in paraffin and selected protic
513 media. Polym. Degrad. Stab. 98(1), 316-324.

514 Rydz, J., Wolna-Stypka, K., Musioł, M., Szeluga, U., Janeczek, H., Kowalczuk, M., 2013b.
515 Further evidence of polylactide degradation in paraffin and in selected protic media. A
516 thermal analysis of eroded polylactide films. Polym. Degrad. Stab. 98, 1450-1457.

517 Sam, S.T., Nuradibah, M.A., Chin, K.M., Hani, N., 2016. Current application and challenges
518 on packaging industry based on natural polymer blending, in: Olatunji, O. (Ed.), Natural
519 polymers: Industry techniques and applications. Springer, Switzerland, pp. 163-185.

520 Shahzad, K., Narodoslawsky, M., Sagir, M., Ali, N., Ali, S., Rashid, M.I., Ismail, I.M.I.,
521 Koller, M., 2017. Techno-economic feasibility of waste biorefinery: Using slaughtering
522 waste streams as starting material for biopolyester production. Waste Manage. 67, 73-85.

523 Sikorska, W., Rydz, J., Wolna-Stypka, K., Musioł, M., Adamus, G., Kwiecień, I, Janeczek,
524 H., Duale, K., Kowalczuk, M., 2017. Forensic engineering of advanced polymeric
525 materials - Part V: Prediction studies of aliphatic-aromatic copolyester and polylactide

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

Sikorska, W., Musioł, M., Nowak, B., Pająk, J., Łabużek, S., Kowalczuk, M., Adamus, G., 2015. Degradability of polylactide and its blend with poly[(R,S)-3-hydroxybutyrate] in industrial composting and compost extract. Int. Biodeter. Biodegr. 101, 32-41.

Sikorska, W., Adamus, G., Dobrzynski, P., Libera, M., Rychter, P., Krucinska, I., Komisarczyk, A., Cristea, M., Kowalczuk, M., 2014. Forensic engineering of advanced polymeric materials – Part II: The effect of the solvent-free non-woven fabrics formation method on the release rate of lactic and glycolic acids from the tin-free poly(lactide-co-glycolide) nonwovens. Polym. Degrad. Stab. 110, 518-528.

Sikorska, W., Richert, J., Rydz, J., Musioł, M., Adamus, G., Janeczek, H., Kowalczuk, M., 2012. Degradability studies of poly (L-lactide) after multi-reprocessing experiments in extruder. Polym. Degrad. Stab. 97, 1891-1897.

Sikorska, W., Dacko, P., Sobota, M., Rydz, J., Musioł, M., Kowalczuk, M., 2008. Degradation study of polymers from renewable resources and their compositions in industrial composting pile. Macromol. Symp. 272, 132-135.

Siyamak, S., Ibrahim, N.A., Abdolmohammadi, S., Yunus, W.M.Z.W., Rahman, M.Z.A.B., 2012. Effect of fiber esterification on fundamental properties of oil palm empty fruit bunch fiber/poly(butylene adipate-co-terephthalate) biocomposites. Int. J. Mol. Sci. 13, 1327-1346.

Swift, G., 2015. Degradable polymers and plastics in landfill sites. Encyclopedia of polymer science and technology 1-13 (published online: 15 September 2015).

Vroman, I., Tighzert, L., 2009. Biodegradable polymers. Materials 2, 307-344.

Whaling, A., Bhardwaj, R., Mohanty, A.K., 2006. Novel talc-filled biodegradable bacterial polyester composites. Ind. Eng. Chem. Res. 45, 7497-7503.

Willett, J.L., Shogren, R.L., 2002. Processing and properties of extruded starch/polymer foams. Polymer 43, 5935-5947.

553 Witt, U., Einig, T., Yamamoto, M., Kleeberg, I., Deckwer, W.D., Muller, R.J., 2001.
554   Biodegradation of aliphatic-aromatic copolyesters: evaluation of the final
555   biodegradability and ecotoxicological impact of degradation intermediates. Chemosphere
556   44(2), 289-299.

557 Yang, H.S., Yoon, J.S., Kim, M.N., 2005. Dependence of biodegradability of plastics in
558   compost on the shape of specimens. Polym. Degrad. Stab. 87, 131-135.

559 Żenkiewicz, M., Richert, A., Malinowski, R., Moraczewski, K., 2013. A comparative analysis
560   of mass losses of some aliphatic polyesters upon enzymatic degradation. Polym. Test. 32,
561   209-214.

1   Marta Musioł[a]*, Wanda Sikorska[a], Henryk Janeczek[a], Wojciech Wałach[a], Anna Hercog[a],

2   Brian Johnston[b], Joanna Rydz[a]

3   [a] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34. M. Curie-

4   Skłodowska St., 41-819 Zabrze, Poland

5   [b] University of Wolverhampton, Faculty of Science and Engineering, Department of Biology,

6   Chemistry and Forensic Science, Wulfruna Street, Wolverhampton, WV1 1SB, UK

7   *mmusiol@cmpw-pan.edu.pl

8

9   **(BIO)DEGRADABLE POLYMERIC MATERIALS FOR A SUSTAINABLE FUTURE-**

10 **PART 1. ORGANIC RECYCLING OF PLA/PBAT BLENDS IN THE FORM OF**

11 **PROTOTYPE PACKAGES WITH LONG SHELF-LIFE**

12

13 **Abstract**

14 Prediction studies of advanced (bio)degradable polymeric materials are crucial when ~~in view~~

15 ~~of~~ their potential applications as compostable products with long shelf-life is considered for

16 today's market. The aim of this study was to determine the effect of the polylactide (PLA)

17 content in the blends of PLA and poly(butylene adipate-*co*-terephthalate) (PBAT) ~~blends~~;,

18 specifically how the material's thickness corresponded to changes that occurred in products

19 during the degradation process. Additionally, the influence of talc on the degradation profile

20 of all samples in all environments was investigated. It was found that, d~~D~~ifferences in the

21 degradation rate of materials tested with a similar content of the PLA component could be

22 caused by differences in their thickness, ~~and/or~~ the presence of commercial additives used

23 during processing or a combination of both. ~~Therefore, the influence of talc on the~~

24 ~~degradation rate of all samples in all types of environments was investigated.~~ The obtained

25 results indicated that the presence of talc may interfere with ~~their~~ materials behaviour towards

26 water and consequently alter their degradation profile.

27

28 **Keywords**: organic recycling, biodegradation, hydrolytic degradation, packages,

29 poly(butylene adipate-*co*-terephthalate), polylactide, talc

30

31 **1. Introduction**

32

33 The key to achieving success and increased presence in the bioeconomy industry is to

34 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 strateg~~yies~~ 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 characteri~~s~~zed 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; Musioł 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 ~~being~~ 340 million tonnes; of this amount 2.05 million tonnes are~~were~~ biobased plastics and 880 000 tonnes ~~were~~ 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~~s~~ of polymers through to the consumer and then through waste management (PLASTICE project) and ~~. R~~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 CO_2, H_2O 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 (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 lines blow film plants applied for low-density polyethylene that can be used for processing PBAT and from that point itwhat 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 characterszed 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 material²s, 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 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 the 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 Musioł 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

4

container system, the samples were incubated for 21 days in three cages at an average temperature of 60 ℃ (± 5 ℃) 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 ℃ 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 ℃. 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 ℃.

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 analysies was ere performed using a Zeiss polarizing microscope (Opton-Axioplan) equipped with a Nikon Coolpix 4500

171 colour digital camera. Pictures were taken at a magnification of 100x. SEM/EDS studies were

172 performed using of a Quanta 250 FEG (FEI Company, USA) high resolution environmental

173 SEM operated at 10 kV acceleration voltages. The samples were observed without a coating,

174 under low vacuum (80 Pa) conditions using a backscattered electron (BSE) detector. Energy

175 dispersive X-ray spectroscopy (EDS) was used for analysis of elemental composition. The

176 spectra were collected by an EDAX Apollo SDD spectrometer with Genesis V6.20 software.

177

178 *2.3.5. Thermal properties*

179 Thermal analysis was carried out on a Mettler-Toledo TGA/DSC STARe System, from 25 to

180 800 °C at a heating rate of 10 °C/min, under a constant flow of 60 mL/min of nitrogen. The

181 obtained TGA data were analyszed using the Mettler-Toledo Star System SW 9.30.

182 Thermal characteristics of the materials studied were also obtained using a TA DSC 2010

183 apparatus (TA Instruments, New Castle, DE). The first calorimetric trace (I-scan, preliminary

184 heating run) in which the thermal history was suppressed, were acquired from -80 °C to 200

185 °C at a heating rate of 20 °C/min, under a nitrogen atmosphere (flow rate = 50 mL/min). The

186 instrument was calibrated with indium and gallium standards. The melting temperature (T_m)

187 was taken as the peak maximum of the melting endotherm.

188

189 *2.3.6. Measurement of the contact angle*

190 Contact angle measurements (Q) for the tested material's surface properties were measured

191 statically using a contact angle goniometer CAM101 (KSV Instruments). The water contact

192 angles were determined in air using the sessile-drop method. A series of images for the water

193 drops (3 μL) were acquired during 15 s, and the average contact angle value was calculated.

194 The contact angle measurements were performed on dry surfaces at 20 °C. An average of five

195 values of contact angles from different parts of the samples was calculated. Two samples of

196 each surface were used for measurements.

197

198 **3. Results and Discussion**

199

200 (Bio)degradation studies were conducted for prototype products made by the Bioerg

201 Company, Poland. The changes of the surface and the changes of the average molar mass of

202 samples (determined by GPC) are indicators of the degradation progress. The thermal

203 characteristics of the materials during the degradation process were determined by TGA and

204 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 $Mg_3Si_4O_{10}(OH)_2$ (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 of 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 ^{1}H 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. The compositional changes (mol%) of samples incubated for 21 days in different environmental conditions, calculated from ^{1}H 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

303 sample. For the F/17 sample, the decrease of PLA content under composting conditions is
304 higher than during the degradation in distilled water at 70 °C after the same time period (see
305 Table 2). Rychter et al. (2010) showed that the mechanism of PBAT degradation in the
306 standardiszed, sandy soil proceeds enzymatically. This may suggest that under industrial
307 composting conditions this mechanism for PBAT as the blend component may have an
308 impact on the degradation process. In the container system, the more favourable conditions
309 for enzymatic degradation exists, thus leaching of PLA degradation products from the blend is
310 facilitated by the degradation of PBAT. Moreover, Oyama et al. (2011) indicated that the
311 products of PLA degradation catalyzes the hydrolytic degradation of the PBAT component in
312 the blend. This conclusion points out that for the blend with a lower content of PLA, a lower
313 hydrolytic degradation rate of PBAT is observed and it results in a lower decrease of M_n
314 during incubation in a container (see Fig. 4). In the case of materials with higher PLA content
315 such as F/40 and T/40 samples, the observed higher M_n changes suggests hydrolytic
316 degradation of both blend components. The obtained results and the compositional changes
317 suggest theat hydrolytic degradation of both components under composting conditions. Thus,
318 in the case of the F/17 sample, the enzymatic degradation of PBAT, especially in the
319 container, may play an important role. Moreover, the changes of the blend composition
320 observed during the degradation process under industrial composting conditions suggests that
321 the degradation of the blend components are more rapid in the container system than in
322 composting pile. This is probably caused by the higher humidity level of the compost in the
323 container system. The static composting pile with natural aeration, located in the open area, is
324 exposed to all weather conditions, which can affect the composting process. In opposition to
325 this, the composting process in the closed system is independent of weather conditions and it
326 allows for better control of the process than in open systems (Kale et al., 2007a).
327 The behavior of the investigated materials during the degradation process in different
328 environments was characteriszed using thermogravimetric analysis. The first differential TGA
329 curve (DTG thermograms) obtained for the materials after 21 days of incubation are plotted in
330 Fig. 5.

331

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

334

335   The thermal effects of both components in the investigated blend samples are similar to each

336   other. This may suggest that these effects partially overlap, which is more visible in the

337   samples with higher PLA content. After degradation in all environments, for the thicker

338   sample (T/40) in the part of the curve in the low temperature region, which corresponds to the

339   PLA, a broader DTG peak than for F/40 was observed. This result confirms the participation

340   of the autocatalytic effect in the T/40 sample's degradation process (Espartero et al. 1996).

341   After the degradation of all the investigated samples in the container system had occurred,the

342   changes in the DTG peak, which corresponds to the PBAT component, was also observed.

343   This indicated that the conclusions, based on the changes in the composition and molar

344   masses of the enzymatic mechanism of PBAT degradation under these conditions are correct

345   with minor contributions of hydrolytic degradation of the investigated material, depending on

346   the PLA content and/or the presence of talc in the samples (Rychter et al., 2010).

347   The DSC results presented in Fig. 6 suggests that the samples studied are not compatible. All

348   the DSC thermograms showed two broad peaks with the maximum value corresponding to

349   both PLA and PBAT component's melting temperatures.

350

351

352   **Fig. 6.** DSC plot of the investigated materials before (0) and after 21 days of incubation in:

353   CP - composting pile, C - container, H - distilled water at 70 °C.

354

355   It is apparent from the DSC traces of the F/40 and T/40 samples after degradation under

356   industrial composting conditions that the melting peak, which corresponds to PLA, is well

357   defined. This result suggests that after degradation in these conditions, more crystalline solid

358   domains with regular crystals were obtained, which in turn results in a sharper melting peak,

359   meaning (the material goes from solid to liquid in a very short temperature range) (Lucas et.

360   all 2008). After degradation in distilled water at 70 °C the PLA melting peak is more

361   expanded. The observed changes in this region for all of the samples could result from the

362   presence of the shorter polymer chains formed *via* the hydrolysis of ester bonds or/and/or the

363   formation of small crystals with irregular structures existing in rigid amorphous domains

364   (Iannace et al. 2001). For the F/17 sample after degradation in the container system, this

365   phenomenon is also observed. This may suggest that under these conditions the regular

366   crystals cannot be properly formed because of the faster leaching of low molar mass PLA

367   oligomers to the degradation medium, which could be facilitated by the degradation of PBAT,

368   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.

Author Contributions

This manuscript was written through contributions from all authors. Marta Musioł 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.

401 **Literature**

402 Adamus, G., Dacko, P., Musioł, M., Sikorska, W., Sobota, M., Biczak, R., Herman, B.,
403   Rychter, P., Krasowska, K., Rutkowska, M., Kowalczuk, M., 2006. Degradation of
404   selected synthetic polyesters in natural conditions. Polimery 51, 539-546 (in Polish).

405 Ahmed, J., Varshney, S., 2011. Polylactides - chemistry, properties and green packaging
406   technology: a review. Int. J. Food Prop. 14(1), 37-58.

407 Bart, J.C.J., 2006. Polymer additive analytics. Industrial practice and case studies. Firenze
408   University Press.

409 Bohlmann, G.M., 2005. General characteristics, processability, industrial applications and
410   market evolution of biodegradable polymers, in: Bastioli, C. (Ed.), Handbook of
411   biodegradable polymers. Rapra, Shawbury, pp. 183-217.

412 Commission delegated regulation (eu) no 1363/2013. http://eur-lex.europa.eu/legal-
413   content/EN/TXT/PDF/?uri=CELEX:32013R1363&from=PL (accessed 28 September
414   2013).

415 Espartero, J.L., Rashkov, I., Li, S.M., Manolova, N., Vert, M., 1996. NMR analysis of low
416   molecular weight poly(lactic acid)s. Macromolecules 29, 3535-3539.

417 Ghanbarzadeh, B., Almasi, H., 2013. Biodegradable polymers, in: Chamy, R., Rosenkranz, F.
418   (Eds.), Biodegradation - Life of science. InTech, Rijeka, pp. 141-185.

419 Höglund, A., Odelius, K., Albertsson, A-C., 2012. Crucial differences in the hydrolytic
420   degradation between industrial polylactide and laboratory-scale poly(L-lactide). ACS
421   Appl. Mater. Interfaces 4, 2788-2793.

422 Iannace, S., Maffezzoli, A., Leo, G., Nicolais, L., 2001. Influence of crystal and amorphous
423   phase morphology on hydrolytic degradation of PLLA subjected to different processing
424   conditions. Polymer 42(8), 3799-3807.

425 Ingrao, C., Tricase, C., Cholewa-Wójcik, A., Kawecka, A., Rana, R., Siracusa, V., 2015.
426   Polylactic acid trays for fresh-food packaging: A Carbon Footprint assessment. Sci. Total
427   Environ. 537, 385-398.

International Standard: ISO 15814. Implants for surgery - copolymers and blends based on polylactide - in vitro degradation testing. International Organization for Standardization, Switzerland, 1999.

Jabeen, N., Majid, I., Nayik, G.A., 2015. Drying kinetics of potato using a self-designed cabinet dryer. Cogent Food Agric. 1(1), 6 pages.

Jiang, Y., Loos, K., 2016. Enzymatic synthesis of biobased polyesters and polyamides. Polymers 8(7), 243.

Jost, V., Kopitzky, R. 2015. Blending of polyhydroxybutyrate-co-valerate with polylactic acid for packaging applications-reflections on miscibility and effects on the mechanical and barrier properties. Chem. Biochem. Eng. Q., 29(2), 221-246.

Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S., Singh, P.S., 2007a. Compostability of bioplastic packaging materials: an overview. Macromol. Biosci. 7(3), 255-277.

Kale, G., Auras, R., Singh, S., Narayan, R., 2007b. Biodegradability of polylactide bottles in real and simulated composting conditions. Polym. Test. 26, 1049-1061.

Kale, G., Auras, R., Singh, S., 2006. Degradation of commercial biodegradable packages under real composting and ambient exposure conditions. J. Polym. Environ. 14, 317-334.

Kijchavengkul, T., Auras, R., Rubino, M., Alvarado, E., Camacho Montero, J.R., Rosales, J.M., 2010. Atmospheric and soil degradation of aliphatic - aromatic polyester films. Polym. Degrad. Stab. 95, 99-107.

Koller, M., Maršálek, L., de Sousa Dias, M. M., Braunegg, G., 2017. Producing microbial polyhydroxyalkanoate (PHA) biopolyesters in a sustainable manner. N. Biotechnol., 37, 24-38.

Lucas, N., Bienaime, C., Belloy, C., Queneudec, M., Silvestre, F., Nava-Saucedo, J-E., 2008. Polymer biodegradation: mechanisms and estimation techniques. - A review. Chemosphere 73(4), 429-442.

454 Musioł, M., Sikorska, W., Adamus, G., Kowalczuk, M., 2016a. Forensic engineering of
455   advanced polymeric materials. Part III - Biodegradation of thermoformed rigid PLA
456   packaging under industrial composting conditions. Waste Manage. 2, 69-76.

457 Musioł, M., Sikorska, W., Kowalczuk, M., Adamus, G., 2016b. The development of
458   sustainable bioplastics for new applications in packaging industry. Int. J. Environ. Agric.
459   Res. 2(2), 117-124.

460 Musioł, M., Sikorska, W., Adamus, G., Janeczek, H., Kowalczuk, M., Rydz, J., 2015
461   (Bio)degradable polymers as a potential material for food packaging: studies on
462   the(bio)degradation process of PLA/(R,S)-PHB rigid foils under industrial composting
463   conditions. Eur. Food Res. Technol. 242, 815-823.

464 Musioł, M.T., Rydz, J., Sikorska, W.J., Rychter, P.R., Kowalczuk, M.M., 2011. A preliminary
465   study of the degradation of selected commercial packaging materials in compost and
466   aqueous environments. Pol. J. Chem. Tech. 13, 55-57.

467 Narodoslawsky, M., Shazad, K., Kollmann, R., Schnitzer, H., 2015. LCA of PHA production
468   - Identifying the ecological potential of bio-plastic. Chem. Biochem. Eng. Q. 29(2), 299-
469   305.

470 Narodoslawsky, M., 2010. Structural prospects and challenges for bio commodity processes.
471   Food Technol. Biotechnol. 48(3), 270-275.

472 News/Press releases. Compostable organic waste bags made of Ecovio[®] approved in
473   Ludwigshafen,   Germany.   http://www.plasticsportal.net/wa/plasticsEU/portal/show/
474   common/plasticsportal_news/2013/13_337 (accessed 20 June 2013).

475 News/Press   releases.   Novamont   buys   Eastman's   'Eastar   Bio'   technology.
476   http://www.icis.com/resources/news/2004/09/08/611549/novamont-buys-eastman-s-
477   eastarbio-technology/ (accessed 08 September 2013).

478 Organisation for Economic Co-operation and Development, 2013. Policies for bioplastics in
479   the context of a bioeconomy. DSTI/STP/BIO(2013)6/FINAL (published online: 24
480   September 2014).

481 Osman, M.J., Ibrahim, N.A., Sharif, J., WanYunus, W.M.Z., 2014. Study on water absorption
482   and biodegradation of polylactic acid/poly (butylene adipate-co-terephthalate)
483   nanocomposite. ChemXpress 5(2), 66-72.

484 Oyama HT, Tanaka Y, Hirai S, Shida S, Kadosaka A. Water-disintegrative and biodegradable
485   blends containing poly(L-lactic acid) and poly(butylene adipate-co-terephthalate). J
486   Polym Sci Part B Polym Phys 2011;49(5):342-354.

487 PLASTiCE project, http://www.plastice.org (accessed 10 October 2016).

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

491
492 PN-Z-15011-3:2001 Municipal solid waste compost - Determination of pH, content of
493   organic substance, organic carbon, nitrogen, phosphorus and potassium.

494 Report European Bioplastics, 2017. Bioplastics market data 2017, http://docs.european-
495   bioplastics.org/publications/market_data/2017/Report_Bioplastics_Market_Data_2017.p
496   df (accessed 30 January 2017)

497 Rotenberg, B., Patel, A.J., Chandler, D., 2011. Molecular explanation for why talc surfaces
498   can be both hydrophilic and hydrophobic. J. Am. Chem. Soc. 133, 20521-20527.

499 Rychter, P., Biczak, R., Herman, B., Zawierucha, I., Musioł, M., Sobota, M., Kowalczuk, M.,
500   2011. Environmental degradation of aromatic-aliphatic polyester blends. Evaluation of
501   degradation products in soil and their phytotoxicological impact. Polish J. Environ. Stud.
502   20, 293-298.

503 Rychter, P., Kawalec, M., Sobota, M., Kurcok, P., Kowalczuk, M., 2010. Study of aliphatic-
504   aromatic copolyester degradation in sandy soil and its ecotoxicological impact.
505   Biomacromolecules 11, 839-847.

506 Rychter, P, Biczak, R., Herman, B., Smyłła, A., Kurcok, P., Adamus, G., Kowalczuk, M.,
507   2006. Environmental degradation of polyester blends containing atactic poly(3-

hydroxybutyrate). Biodegradation in soil and ecotoxicological impact. Biomacromolecules 7, 3125-3131.

Rydz, J., Musioł, M., Zawidlak-Węgrzyńska, B., Sikorska, W., 2018. Present and future of (bio)degradable polymers for food packaging applications, in: Grumezescu, A.M., Holban, A.M. (Eds.), Handbook of food bioengineering. Elsevier, Romania, pp. 429-465.

Rydz, J., Sikorska, W., Kyulavska, M., Christova, D., 2015a. Polyester-based (bio)degradable polymers as environmentally friendly materials for sustainable development. Int. J. Mol. Sci. 16(1), 564-596.

Rydz, J., Wolna-Stypka, K., Adamus, G., Janeczek, H., Musioł, M., Sobota, M., Marcinkowski, A., Krzan, A., Kowalczuk, M., 2015b. 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. 29(2), 247-259.

Rydz, J., Adamus, G., Wolna-Stypka, K., Marcinkowski, A., Misiurska-Marczak, M., Kowalczuk, M.M., 2013a. Degradation of polylactide in paraffin and selected protic media. Polym. Degrad. Stab. 98(1), 316-324.

Rydz, J., Wolna-Stypka, K., Musioł, M., Szeluga, U., Janeczek, H., Kowalczuk, M., 2013b. Further evidence of polylactide degradation in paraffin and in selected protic media. A thermal analysis of eroded polylactide films. Polym. Degrad. Stab. 98, 1450-1457.

Sam, S.T., Nuradibah, M.A., Chin, K.M., Hani, N., 2016. Current application and challenges on packaging industry based on natural polymer blending, in: Olatunji, O. (Ed.), Natural polymers: Industry techniques and applications. Springer, Switzerland, pp. 163-185.

Shahzad, K., Narodoslawsky, M., Sagir, M., Ali, N., Ali, S., Rashid, M.I., Ismail, I.M.I., Koller, M., 2017. Techno-economic feasibility of waste biorefinery: Using slaughtering waste streams as starting material for biopolyester production. Waste Manage. 67, 73-85.

Sikorska, W., Rydz, J., Wolna-Stypka, K., Musioł, M., Adamus, G., Kwiecień, I, Janeczek, H., Duale, K., Kowalczuk, M., 2017. Forensic engineering of advanced polymeric materials - Part V: Prediction studies of aliphatic-aromatic copolyester and polylactide

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

537 Sikorska, W., Musioł, M., Nowak, B., Pająk, J., Łabużek, S., Kowalczuk, M., Adamus, G.,
538 2015. Degradability of polylactide and its blend with poly[(R,S)-3-hydroxybutyrate] in
539 industrial composting and compost extract. Int. Biodeter. Biodegr. 101, 32-41.

540 Sikorska, W., Adamus, G., Dobrzynski, P., Libera, M., Rychter, P., Krucinska, I.,
541 Komisarczyk, A., Cristea, M., Kowalczuk, M., 2014. Forensic engineering of advanced
542 polymeric materials − Part II: The effect of the solvent-free non-woven fabrics formation
543 method on the release rate of lactic and glycolic acids from the tin-free poly(lactide-co-
544 glycolide) nonwovens. Polym. Degrad. Stab. 110, 518-528.

545 Sikorska, W., Richert, J., Rydz, J., Musioł, M., Adamus, G., Janeczek, H., Kowalczuk, M.,
546 2012. Degradability studies of poly (L-lactide) after multi-reprocessing experiments in
547 extruder. Polym. Degrad. Stab. 97, 1891-1897.

548 Sikorska, W., Dacko, P., Sobota, M., Rydz, J., Musioł, M., Kowalczuk, M., 2008.
549 Degradation study of polymers from renewable resources and their compositions in
550 industrial composting pile. Macromol. Symp. 272, 132-135.

551 Siyamak, S., Ibrahim, N.A., Abdolmohammadi, S., Yunus, W.M.Z.W., Rahman, M.Z.A.B.,
552 2012. Effect of fiber esterification on fundamental properties of oil palm empty fruit
553 bunch fiber/poly(butylene adipate-co-terephthalate) biocomposites. Int. J. Mol. Sci. 13,
554 1327-1346.

555 Swift, G., 2015. Degradable polymers and plastics in landfill sites. Encyclopedia of polymer
556 science and technology 1-13 (published online: 15 September 2015).

557 Vroman, I., Tighzert, L., 2009. Biodegradable polymers. Materials 2, 307-344.

558 Whaling, A., Bhardwaj, R., Mohanty, A.K., 2006. Novel talc-filled biodegradable bacterial
559 polyester composites. Ind. Eng. Chem. Res. 45, 7497-7503.

560 Willett, J.L., Shogren, R.L., 2002. Processing and properties of extruded starch/polymer
561 foams. Polymer 43, 5935-5947.

562   Witt, U., Einig, T., Yamamoto, M., Kleeberg, I., Deckwer, W.D., Muller, R.J., 2001.
563   Biodegradation of aliphatic-aromatic copolyesters: evaluation of the final
564   biodegradability and ecotoxicological impact of degradation intermediates. Chemosphere
565   44(2), 289-299.

566   Yang, H.S., Yoon, J.S., Kim, M.N., 2005. Dependence of biodegradability of plastics in
567   compost on the shape of specimens. Polym. Degrad. Stab. 87, 131-135.

568   Żenkiewicz, M., Richert, A., Malinowski, R., Moraczewski, K., 2013. A comparative analysis
569   of mass losses of some aliphatic polyesters upon enzymatic degradation. Polym. Test. 32,
570   209-214.

Table 1

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

Product type	Sample name	PLA content [mol%]	Thickness [mm]
Film	F/17	17±0.5	0.02 ±0.01
	F/40	40±1.0	0.03±0.01
Disposable bag market	T/40	40±0.5	0.10±0.01

Product type	Sample name	PLA content [mol%]	Thickness [mm]
	F/17	17±0.5	0.02 ±0.01

Table 2

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

Sample name	Degradation environment		
	water	pile	container
F/17	14±1.0	12±0.5	6±0.5
F/40	34±0.5	39±0.5	36±1.0
T/40	35±1.0	40±0.5	37±1.0

Figure 1
Click here to download high resolution image
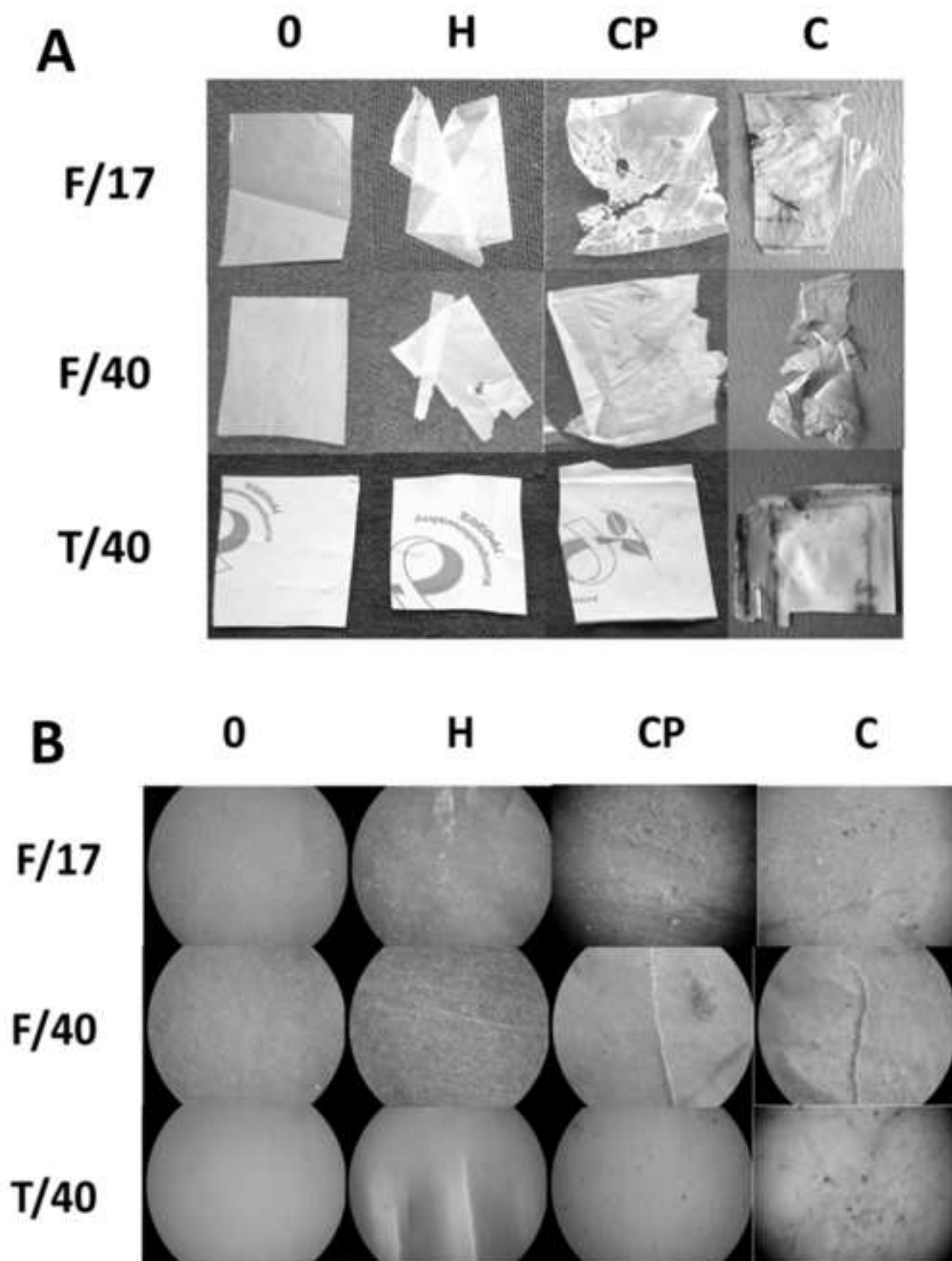
Figure 2
Click here to download high resolution image
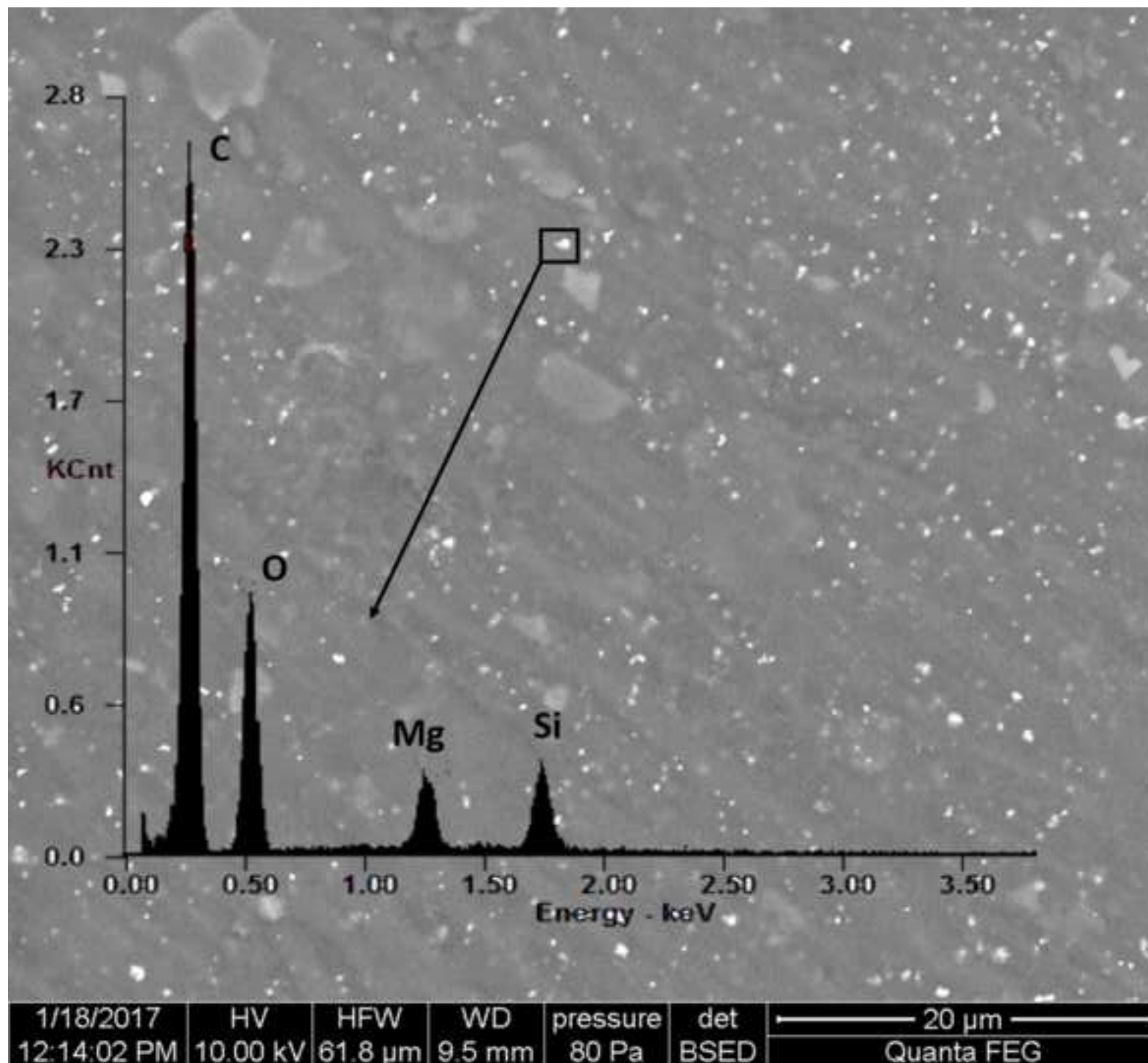
Figure 3
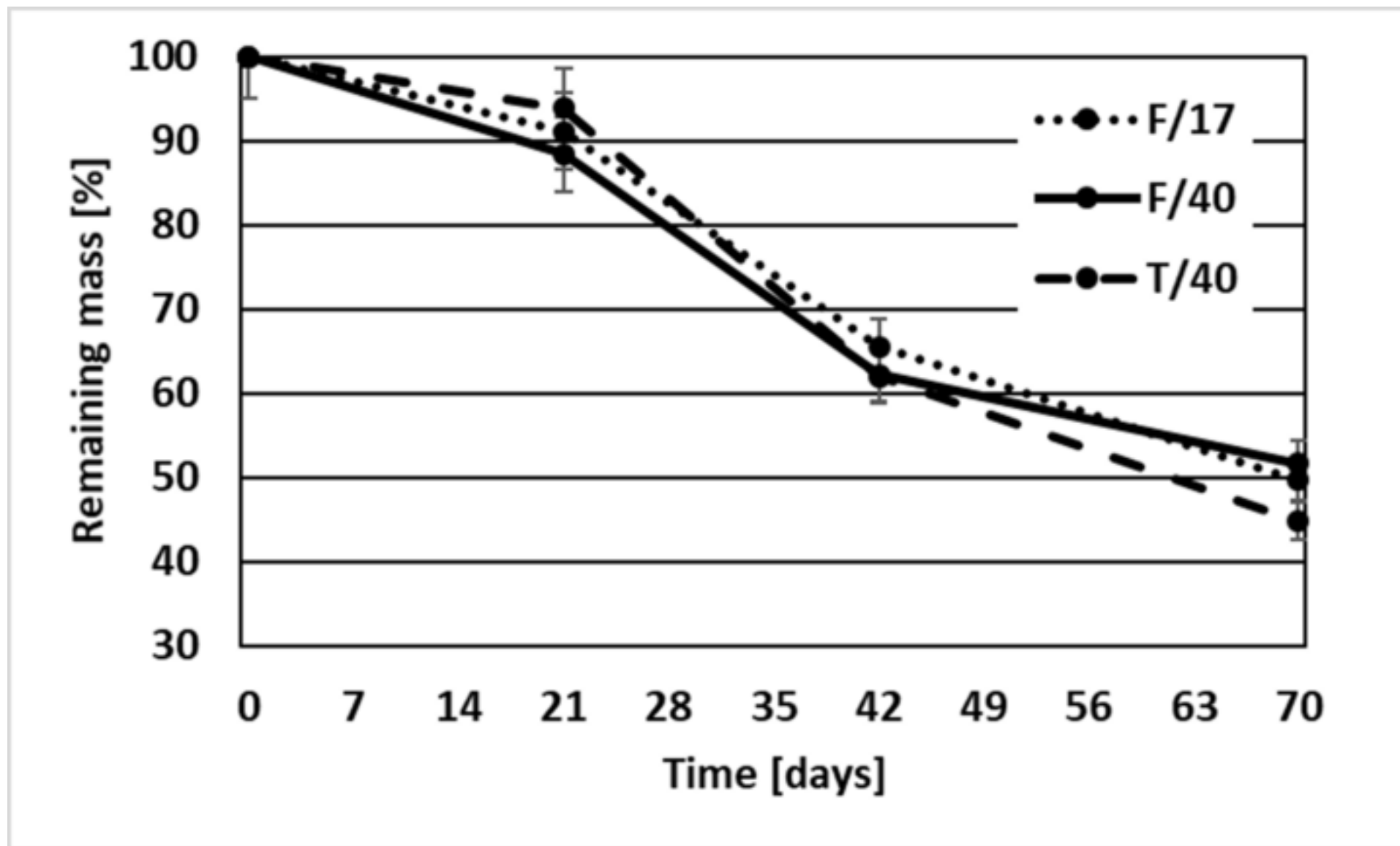**Click here to download high resolution image**

Figure 4
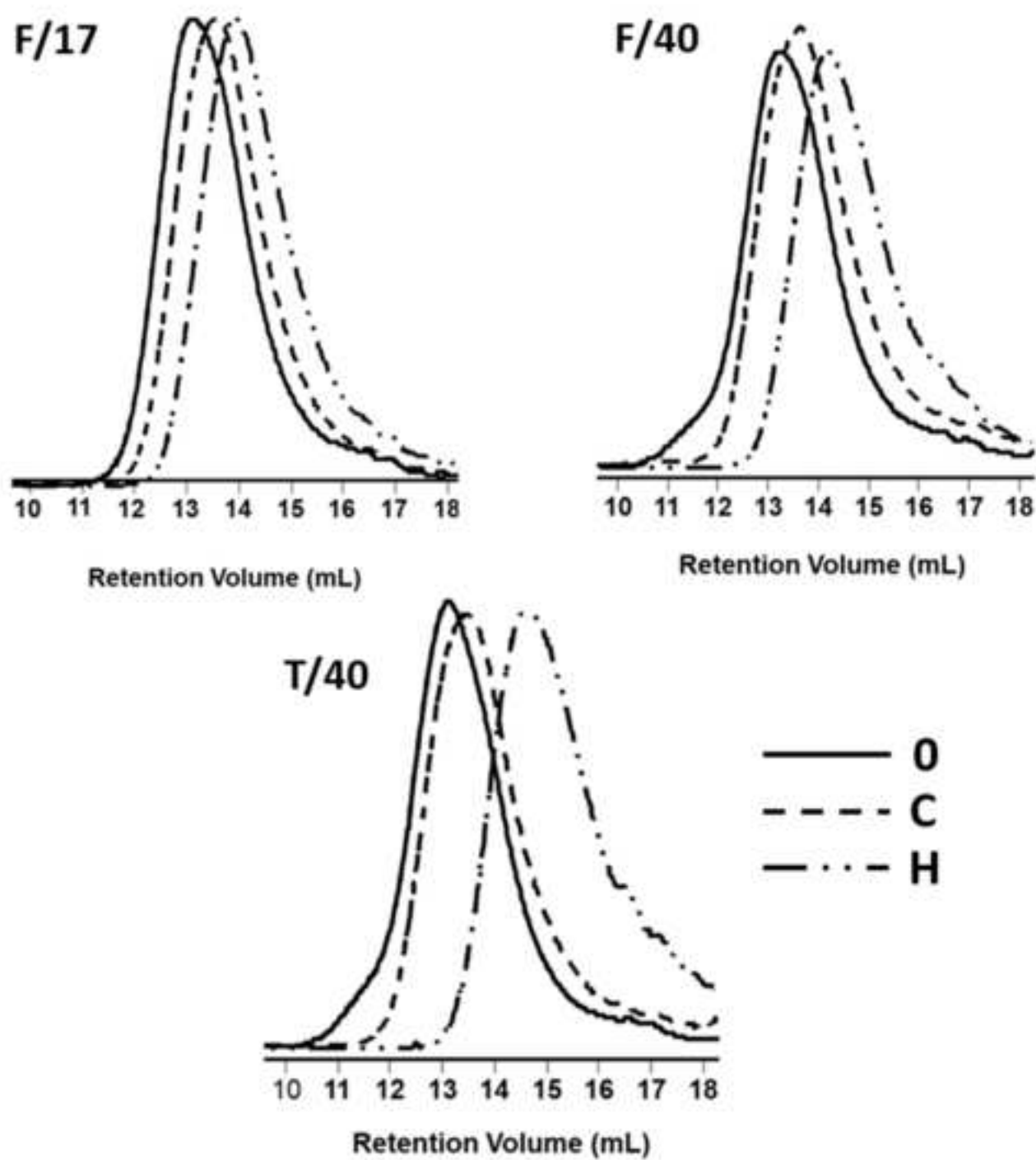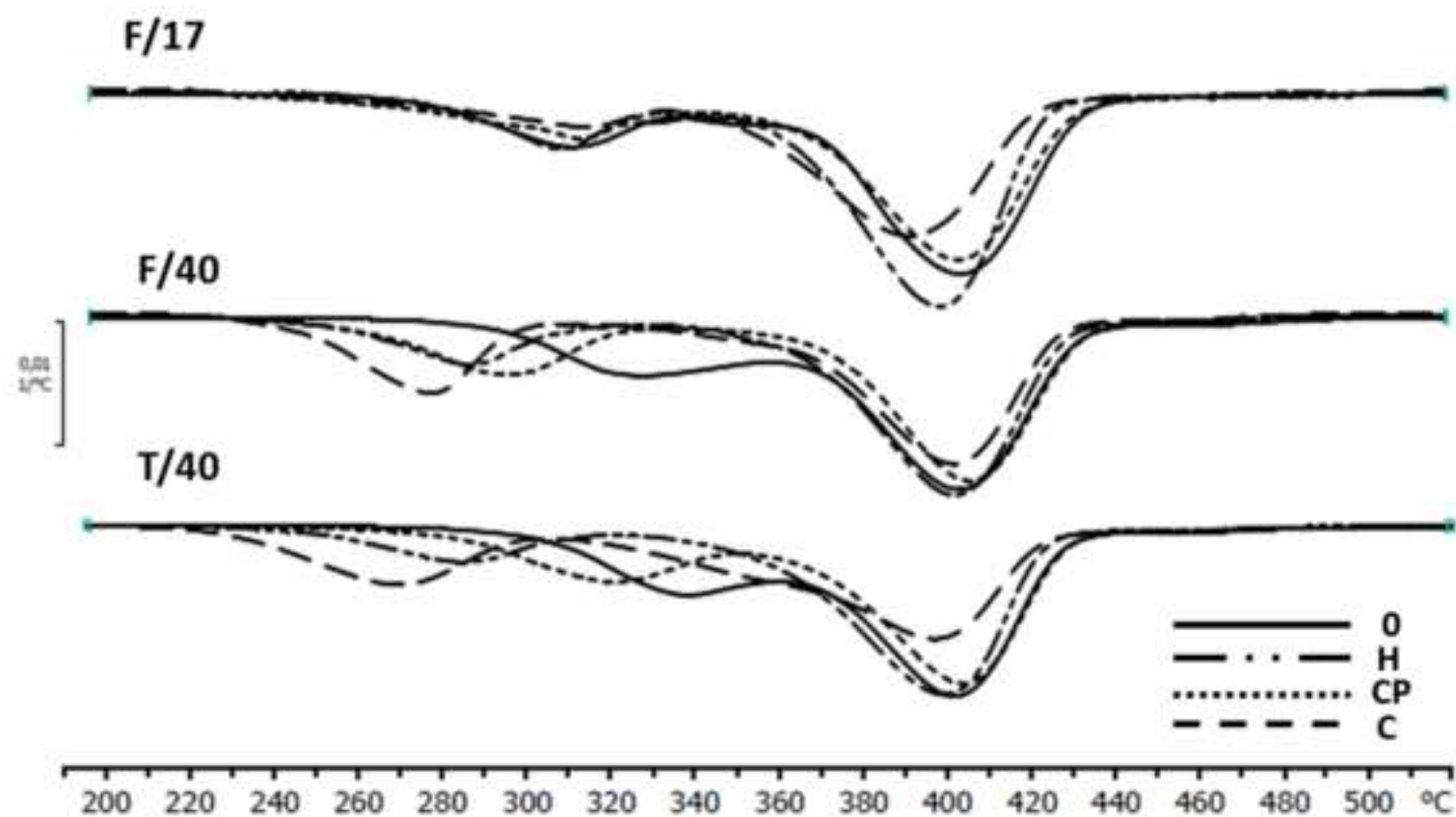**Click here to download high resolution image**

Figure 5

Figure 6
Click here to download high resolution image