Article

Molecular and Supramolecular Changes in Polybutylene Succinate (PBS) and Polybutylene Succinate Adipate (PBSA) Copolymer during Degradation in Various Environmental Conditions

Michał Puchalski*[1], Grzegorz Szparaga[1], Tadeusz Biela[2], Agnieszka Gutowska[3,4], Sławomir Sztajnowski[1] and Izabella Krucińska[1]

[1] Lodz University of Technology, Faculty of Material Technologies and Textile Design, Department of Material and Commodity Sciences and Textile Metrology, Centre of Advanced Technologies of Human-Friendly Textiles "Pro Humano Tex", Zeromskiego 116, 90-924 Lodz, Poland,
[2] Department of Polymer Chemistry, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-301 Lodz, Poland
[3] Institute of Biopolymers and Chemical Fibres, Department of Synthetic Fibers, Skłodowskiej–Curie 19/27, 90-570 Lodz, Poland
[4] Institute of Security Technologies "MORATEX", Sklodowskiej-Curie 3, 90-505 Lodz, Poland

* Correspondence: michal.puchalski@p.lodz.pl; Tel.: +48-42-631-33-22

Abstract: In this paper, the influence of the various degradation conditions, on the molecular and supramolecular structure of polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA) copolymer during degradation time is described. Experiment was carried out by the use injection molded samples and normalized conditions of biodegradation in soil, composting and artificial weathering. Materials were studied by using size-exclusion chromatography (SEC) coupled with multiangle laser light scattering (MALLS) detection and wide-angle X-ray diffraction (WAXD). Additionally, the physical and mechanical properties of the samples were determined. The performed experiments clearly show difference impact of selected degradation condition on the macroscopic, supramolecular and molecular parameters of studied aliphatic polyesters. The structural changes in PBS and PBSA explain the observed changes in the physical and mechanical properties of the obtained injection molded samples.

Keywords: PBS; PBSA; WAXD, SEC-MALLS, degradation, composting, artificial weathering

---

1. Introduction

In recent years, pro-ecological trends in waste reduction have led to the substitution of durable polymers with biodegradable polymers. For this, thermoplastic aliphatic polyesters are promising alternatives [1, 2]. In this group of polymers, polybutylene succinate (PBS) is an interesting material from an application standpoint, as its mechanical properties are similar to those of popular polymers such as polypropylene (PP) [3].

Polybutylene succinate (PBS) is a biodegradable aliphatic polyester produced by the polycondensation of succinic acid (SA) and 1,4-butanediol (BD) [4]. Due to the high crystallinity and good thermal properties of the homopolymers, a copolymer of polybutylene succinate (PBS) and polybutylene adipate (PBA) has been used in selected applications, such as packaging. The physical properties and crystalline structure of the polybutylene succinate adipate (PBSA) copolymer strongly depend on the concentration of the polymer compounds. Moreover, the PBSA copolymer is characterized by a higher degradability by enzymatic processes compared with other materials due to its lower crystallinity [5].

For many years, PBS and PBSA have been produced from petrochemical sources by Showa Highpolymer (Shanghai, China). The polymer, which has the trade name Bionolle, is characterized by its similar processability to that of conventional resins such as polyethylene. Bionolle is one of the most suitable materials for processing into films, which can then be utilized for agricultural purposes, shopping bags, compost bags, and so on. Showa Highpolymer has succeeded in producing a compound of Bionolle and starch that not only has similar properties to homogeneous Bionolle but is also environmentally friendly [6-8].

The lack renewability and the rising price of fossil resources have limited the use of petrochemical succinic acid for a wide range of applications. Consequently, the natural next step was to develop a synthetic method for bio-succinic acid from a renewable source, such as biomass. The yeast- or bacteria-based production of succinic acid and possibility to source 1,4-butanediol from ecological methods make PBS and its copolymers attractive biodegradable polymers that are completely produced from renewable resources [9-11].

Currently, research on this topic is related to the search for new applications of PBS, for example, the development of novel materials for ecological agriculture purposes. Developed materials such as mulching nonwovens and pots produced from nonwovens are interesting alternatives to polypropylene products [12,13]. Another area of work is the use of polybutylene succinate as an additive to plasticize other biodegradable polymers, such as PLA [14-16]. Research is therefore concerned with the search for new applications for this aliphatic polyester [17-19].

On the other hand, research has focused on the analysis of the degradation of PBS, PBA and their copolymers by the examination of new degradation conditions, enzymes and microorganisms [5, 20-22]. This topic is still developing and continues to expand the understanding of this polymer and other aliphatic polyesters. The impacts of the degradation process on weight loss, the decrease in the molar mass and changes in the mechanical properties have been evaluated [23, 24]. The kinetics of the degradation process have also been analyzed [25]. However, there are few results for the assessment of changes in the supramolecular structure during the PBS degradation process [26]. For other aliphatic polyesters (e.g., PLA), such changes were observed and were responsible, inter alia, for a decrease in the mechanical properties [27].

In this study, the degradation of commercially available PBS and PBSA copolymer in three various regimes, biodegradation in compost, biodegradation in soil and artificial weathering, was performed. The experiment was carried out under laboratory conditions according to the obligatory standard. For complete analysis, the change in the studied samples during degradation was analyzed on the macroscopic, supramolecular and molecular scales. The estimation of mass loss and change in the mechanical properties was carried out according to the obligatory standard, while supramolecular and molecular parameters were investigated by using wide-angle X-ray diffraction (WAXD) and size-exclusion chromatography (SEC) coupled with multiangle laser light scattering (MALLS) detection.

2. Materials and Methods

2.1. Materials

In the experiments, the commercially available polybutylene succinate (PBS) Bionolle 1020 MD and polybutylene succinate adipate (PBSA) copolymer Bionolle 3020 MD were purchased from Showa Denko K.K. (Japan). For the tensile test, the samples were formed into dog-bone shaped specimens by the use of an injection molding machine (Allrounder 420C, Arburg, Germany) according to the ISO-527-2-1A standard. The polymer materials were formed at 180°C (PBS, 1020 MD) and 170°C (PBSA, 3020 MD).

2.2. Degradation environment

2.2.1. Laboratory biodegradation

The laboratory biodegradation of the PBS and PBSA samples was conducted under controlled conditions according to the International Standard PN-EN ISO 20200:2016 and European Standards PN-EN 14806:2010 and PN-EN 14045:2005. The experiment was carried out using common commercially available garden soil with a pH of 6.0-6.5 and 1.8 × 107 cfu/g microorganisms and compost from an industrial compost prism (Municipal Services Company of the city of Łódź) with a pH of 7 and 3.2×107 cfu/g microorganisms [12, 28]. The studied samples were biodegraded in the garden soil at a temperature of 30±2°C, and the medium had a moisture content of 55.6%, while the samples were biodegraded in compost at a temperature of 58±2°C, and the medium had a moisture content of 53.1%, which was in line with the adopted standards. The biodegradation process were controlled to have defined time intervals (1, 4, 8, 12, 16, 20 and 24 weeks). During the experiment, moisture was replenished to the initial value with water. After a defined incubation time, the samples were dried to constant weight, and the mass loss was estimated. Each sample was tested 3 times. The resulting variation in the results of the biodegradation tests was below 10%.

2.2.2. Laboratory artificial weathering

The laboratory artificial weathering of the studied PBS and PBSA samples was carried out in a QUV chamber according to standard PN EN ISO 4892-3 based on Technical Report TR 010 ed. May 2004 “Exposure procedure for artificial weathering”. The weathering process was performed in cycles, irradiating the samples with a light intensity of 0.76 W/m^2 by UVA-340 nm radiation under the following conditions:

- 8 hours of exposure – chamber temperature (ChT) 50°C, relative humidity (RH) 40%;
- 4 hours of artificial rainfall with demineralized water and no exposure – ChT = 20°C.

The samples were weathered for defined time intervals, 45, 90, 180, 360, 540, 720, 900, 1080, 1260, 1440 and 1800 hours, where the 720 hour interval corresponds to the natural exposure of a sample over 1 year in a moderate climate (e.g., in Poland).

2.2. Mechanical properties

The mechanical parameters of the PBS and PBSA samples that did not fall apart during degradation were measured using an Instron 5511 mechanical testing machine (Instron, USA). The tests were carried out according to the PN-EN ISO 527-2:2012 standard.

2.3. SEC-MALLS method

The molar mass (M_n) and dispersity ($Đ$) of the studied PBS and PBSA materials were analyzed by size-exclusion chromatography (SEC) coupled with multiangle laser light scattering (MALLS) detection. The SEC–MALLS instrument was composed of an Agilent 1100 isocratic pump, an auto-sampler, a degasser, a thermostatic box for columns, a MALLS DAWN HELEOS-II photometer (Wyatt Technology Corporation, Santa Barbara, CA) and an Optilab T-rEX differential refractometer. The ASTRA 4.90.07 software package (Wyatt Technology Corporation) was used for data collection and processing. Two PLGel 5 μm MIXD-C columns were used for separation. The samples were injected as a methylene chloride solution. The volume of the injection loop was 100 μm^3. Methylene chloride was used as the mobile phase at a flow rate of 0.8 $cm^3 \cdot min^{-1}$. The calibration of the DAWN HELEOS-II photometer was performed using p.a.-grade toluene, and normalization was performed using a polystyrene standard (M_n = 30,000 g/mol). The measurements were conducted at room temperature.

2.4. WAXS method

The changes in the supramolecular structures of the PBS and PBSA samples during degradation were investigated by wide-angle X-ray diffraction scattering (WAXS) using an X’Pert PRO

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 26 January 2018 doi:10.20944/preprints201801.0254.v1

Peer-reviewed version available at *Polymers* **2018**, *10*, 251; doi:10.3390/polym10030251

diffractometer (CuKα source, λ = 0.154 nm) from PANalytical (Netherlands). The X-ray diffractograms were recorded in the 2θ range of 5° to 60° with a step of 0.05°. The obtained WAXS data were analyzed numerically using the WAXSFIT software [29].

3. Results and Discussion

3.1. Analysis of the physical properties of the studied materials after degradation

The physical changes in the structures of the studied materials were directly observed and recorded photographically. In Figure 1, a collection of selected photographs of the degradation processes occurring in various conditions is presented. According to these photographs, the most degrading medium was compost. During PBSA biodegradation in compost, the tested sample began to fragment after 4 weeks, and PBS began to fragment after 6 weeks. The other degradation conditions applied in the investigation did not result in fragmentation of the studied materials. Matting of the sample surface and additional color changes are the only visible changes resulting from artificial weathering.

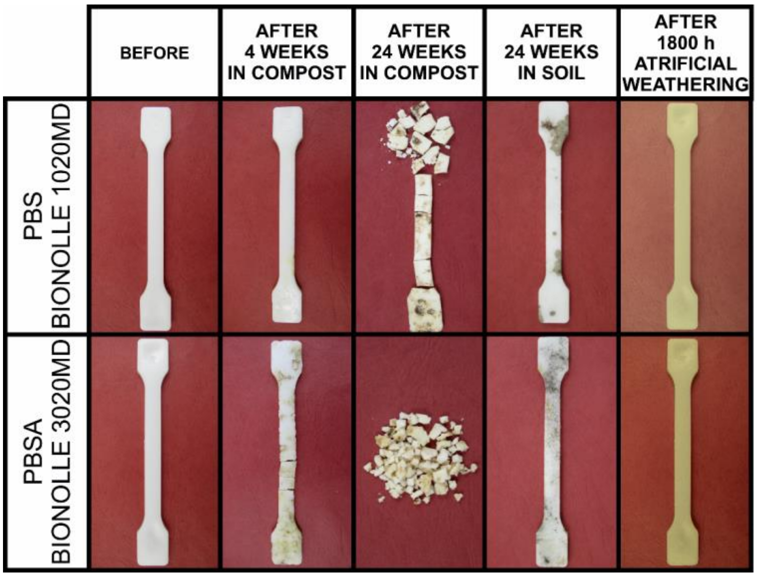

Figure 1. Photographs of the investigated samples before and after degradation.

The most often analyzed macroscopic factor in material degradation assessments is the mass loss. In Figure 2, the mass changes of the studied PBS and PBSA samples as a function of degradation time are shown. The most visible mass loss was measured for the samples biodegraded in compost. (Fig. 1a), while the weakest initiator of mass loss was artificial weathering, where the maximum mass loss was only around 1% for both studied materials (Fig. 1c). The insignificant changes in the sample mass during aging under simulated atmospheric conditions seems to be a result of the absence of its direct physical contact with the degrading medium. In the soil or in compost, the degraded products probably diffuse from the surface layer into the environment, which is observed as a decrease in mass. Furthermore, in compost, a visible strong mass loss also results from the reaction with enzymes that support the erosion of the surface of the studied material.

Analysis of the difference between both studied Bionolle polymers clearly shows a higher mass loss from the PBSA material than the PBS material during the same time. It is worth noting that the PBS polymer lost a significant amount of mass only during biodegradation in compost, and other initiators did not cause a decrease in its mass.

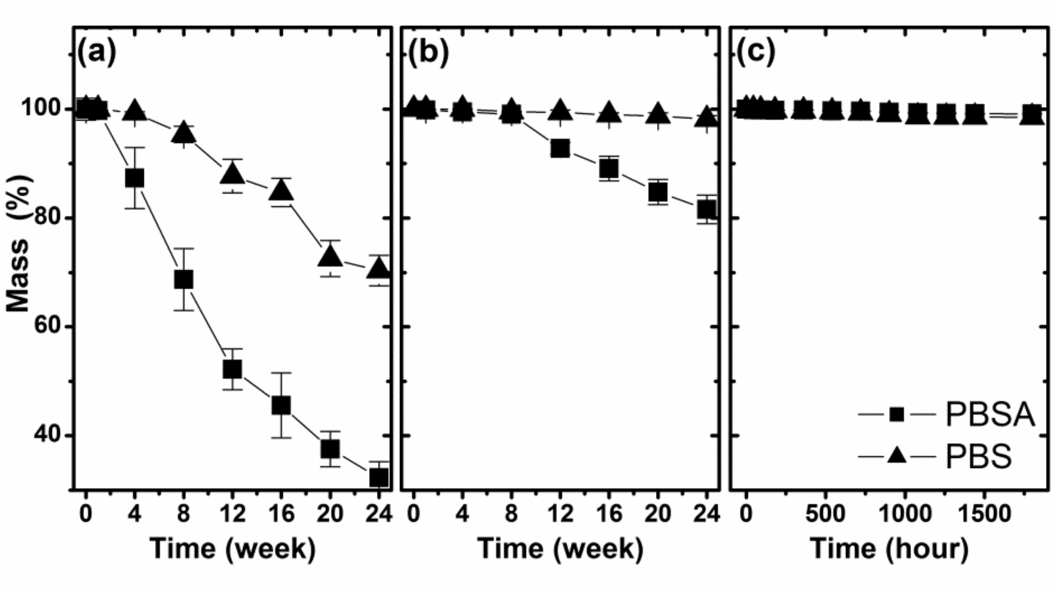

Figure 2. The mass changes of the studied samples during degradation in selected environments: (**a**) biodegradation in compost, (**b**) biodegradation in soil and (**c**) artificial weathering.

The next step in the macroscopic analysis of physical changes of the studied samples was the investigation of their mechanical properties. In Figure 3, the strain and elongation at break as a function of degradation time is shown. As it is seen, there is a lack of information about changes in the mechanical properties of the studied samples during biodegradation in compost. Samples that were composted for more than 1 or 4 weeks were fragmented into smaller pieces, which prevented mechanical testing (Fig. 1). The strain and elongation at break of PBS after 4 weeks (maximum time after which the sample is not fragmented) decreased from 34.8 MPa to 12.7 MPa and 321.8% to 1.7% respectively, while for PBSA, after 1 week, these values decreased from 28.6 MPa to 21.8 MPa and from 757.9% to 196.1%. These results indicate the strong degradation of both polymers in compost, which is probably the effect of its composition being more complex than soil from a microbiological (enzymatic) point of view. The changes in the mechanical properties of the studied polymers as a function of degradation time clearly show a large decrease in the elasticity of the materials during the degradation process, both in the biodegradation process in soil and in the irradiation process of artificial weathering, as presented in Figure 3. Furthermore, as a result of the artificial weathering process, the strength of both studied polymers was significantly reduced (Fig. 3b). Considering the lack of mass loss and matting of the sample surface, it can be concluded that the structure of the polymers changed on a molecular and supramolecular level, as discussed in the next part of the paper.

Slightly different changes in the strain of the polymers were observed in the biodegradation process in soil (Fig. 3a). For PBS and PBSA, the rate of change was lower than during degradation under artificial weathering conditions. Based on the analysis of the estimated macroscopic factors, the biodegradation process in soil was the least effective among the tested methods.

Peer-reviewed version available at Polymers 2018, 10, 251; doi:10.3390/polym10030251

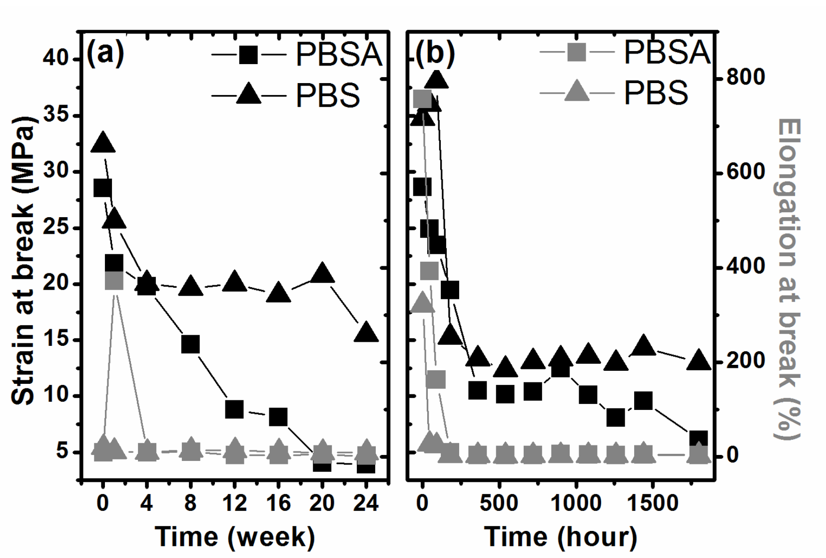

Figure 3. The changes in the mechanical properties of the studied samples during degradation in selected environments: (a) biodegradation in soil and (c) artificial weathering.

3.2. Changes in the molar mass and dispersity of the studied materials during degradation

The molecular parameters (M_n and $M_w/M_n = Đ$) of the studied polymers were analyzed using the SEC-MALLS method. In Figure 4, the number-average molar mass (M_n) and dispersity ($Đ$) [31] of the studied samples as a function of degradation time under the selected conditions are presented. The most visible change in the molecular parameters of the studied polymers was observed for the samples degraded by the artificial weathering process. Exposure of the sample to UV radiation, high relative humidity and heat resulted in a decrease in the number-average molar weight and an increase in the dispersity of both studied polymers (Fig. 4c). During this process, the value of M_n decreased from 37.4 kg/mol and 37.8 kg/mol to 11.0 kg/mol and 12.1 kg/mol for PBS and PBSA, respectively. However, the dispersity increased from 1.65-1.69 to 2.8-3.0. The obtained results suggest the strong influence of artificial weathering on the molecular parameters of both polymers.

The number-average molar mass dependence on the degradation time during artificial weathering was almost linear. A similar linear tendency was also observed for the dispersity, but this molecular parameter increased with degradation time. Artificial weathering resulted in a random process for the decomposition of PBS and PBSA macromolecules.

Obviously different results were obtained for the biodegradation of both polymers in compost: the polymer molecular weight decreased accompanied by a reduction in the dispersity. The loss of Mn as a result of degradation is a typical phenomenon in this process, but the decreased dispersity suggests another degradation mechanism than that observed for artificial weathering. For up to 12 weeks, the dispersity was approximately 1.60 for both studied polymers; however, during the next interval of biodegradation, an insignificant decrease was observed, and finally, after 24 weeks, the dispersities of PBS and PBSA were 1.20 and 1.43, respectively. Most likely, at least two mechanisms operate during biodegradation in compost: the relatively slow hydrolysis of higher molar mass polymers and the faster enzymatic etching of oligomers. It is important to emphasize that enzymes are capable of etching only polymers with a sufficiently low molar mass. Therefore, this process is not random, as is degradation during artificial weathering. Hydrolysis leads to a decrease in the overall molar mass, but enzymatic etching eliminates the oligomeric fraction from the samples relatively quickly. As a consequence, both the molar mass and dispersity are reduced. Additionally, the decrease in M_n as a function of degradation time was non-linear and showed an almost exponential decrease. Moreover, the obtained results showed that the PBSA copolymer was more resistant to degradation in compost than the PBS polymer.

The degradation process was also analyzed in soil (Fig. 4b). Biodegradation of the studied polymers in soil gave similar results to the biodegradation in compost, but the changes in the molecular parameters were less intense. The M_n decreased, but without significant changes in dispersity, which indicates the random degradation of polymer chains with uniform molecular weight loss in all polymer fractions. At the end of the experiment, the M_n values of PBS and PBSA were 23 kg/mol and 31 kg/mol, respectively. As clearly shown, PBSA was more resistant to degradation in soil, and a visible decrease in the molar mass was observed only after 16 weeks. The profile of the molar mass loss of PBS as a function of degradation time was similar to that for biodegradation in compost. The main visible change in M_n was observed only during the initial period of biodegradation, up to 4 weeks.

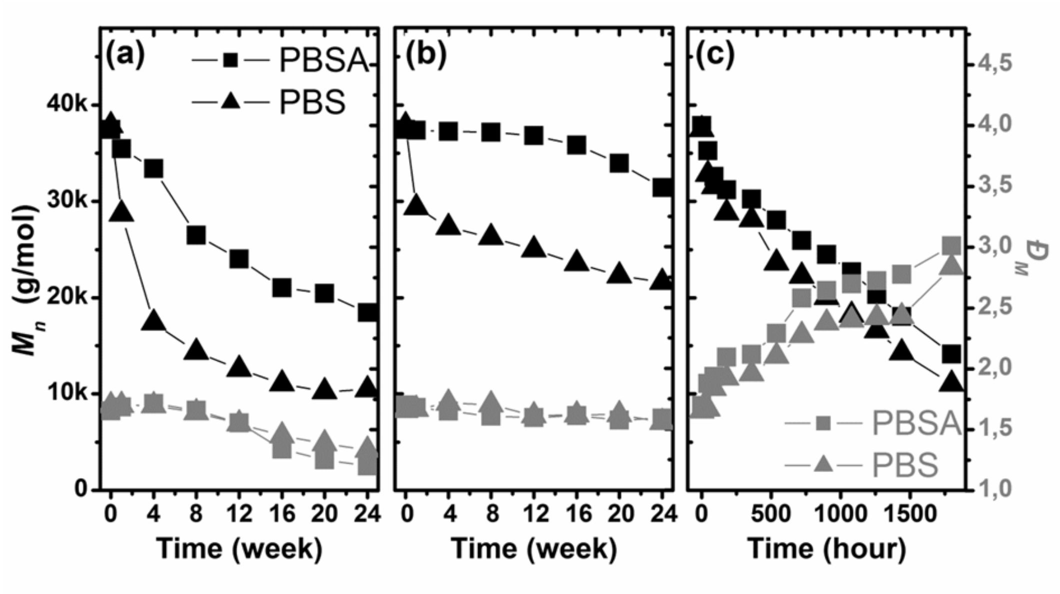

Figure 4. Changes in M_n (black symbols) and dispersity (gray symbols) of the studied samples during degradation in selected environments: (**a**) biodegradation in compost, (**b**) biodegradation in soil and (**c**) artificial weathering.

3.3. Analysis of the supramolecular structure of the studied materials after degradation

The presented SEC-MALLS results showed the influence of various conditions on the mechanism of polymer degradation and on the changes in the molecular structures of the studied polymers. To estimate the changes in the supramolecular structure of the materials during degradation, wide-angle X-ray diffraction was employed. In Figures 5, examples of the X-ray diffraction profiles of both studied polymers are shown. The X-ray diffraction peaks at 2θ = 19.7°, 22.1°, 22.8°, 26.2° and 29.1°, corresponding to the $(11\bar{1})/(002)$, (012), (110), $(12\bar{1})$ and (111) planes of the poly(butylene) succinate monoclinic crystal lattice, were clearly visible. The diffraction patterns do not give much information about the poly(butylene) adipate crystalline structure. The strongest diffraction peaks at 2θ = 17.6° and 21.7°, corresponding to the (002) and (110) planes of PBA, are not detectable. This result indicates that a low content (<25% wt.) of poly(butylene) adipate is present in studied copolymer [22].

Peer-reviewed version available at Polymers 2018, 10, 251; doi:10.3390/polym10030251

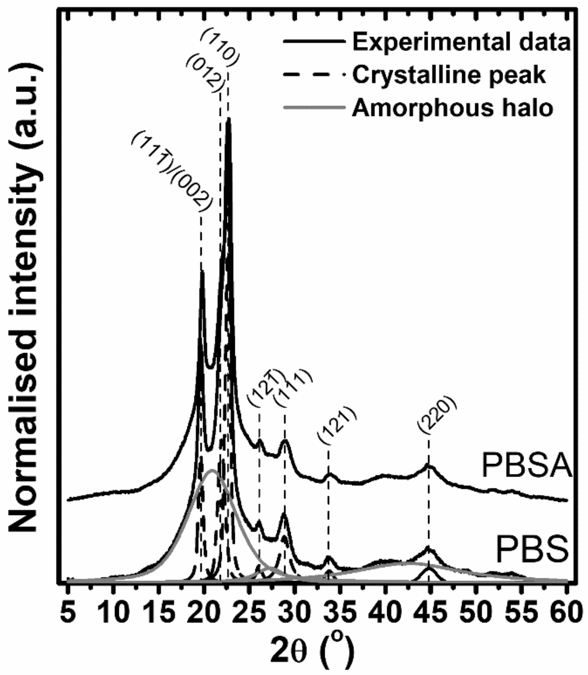

Figure 5. X-ray diffraction profiles of PBS and PBSA samples with deconvolution to the amorphous and crystalline compounds.

Due to slight changes in the X-ray profiles of the polymers as a result of the degradation process, numerical analysis of the profiles was performed to estimate the quantitative influence of degradation on the supramolecular structure of the studied materials. For this analysis, deconvolution of the experimental data to the amorphous halo and crystalline peaks was performed according to Hindeleh and Johnson's method (Fig. 5). The X-ray diffraction patterns were directly analyzed to obtain the crystalline phase content according to equation (1):

$$\chi_C = \frac{A_C}{A_C + A_A} \tag{1}$$

where A_A and A_C are the integrated areas calculated under the amorphous and crystalline curves, respectively.

In Figure 6, the degree of crystallinity of the studied polymers as a function of degradation time under various conditions is presented. As clearly shown, the largest change in the crystallinity was observed after biodegradation in compost. The degree of crystallinity (35% for PBS and 27% for PBSA) increased to 52% for both materials. Notably, during biodegradation in compost, the polymer crystallized almost linearly. This phenomenon was not observed in the other tested degradation conditions, where the degree of crystallinity increased significantly in the initial period and then did not change significantly. The maximum degree of crystallinity for PBS was approximately 40% in both conditions, while for PBSA, this value was approximately 37% for biodegradation in soil and approximately 40% for artificial weathering. The presented results of the change in crystallinity partly correlate with the changes in the molecular structures of the polymer. The decrease in dispersity with decreasing number-average molar mass during biodegradation in compost caused the creation of the crystalline phase; on the other hand, the increase in Đ with decreasing M_n during artificial weathering was not favorable for the crystallization process. In accordance with the results, the crystallinity is affected not only by a decrease in the molar mass but also by a change in the dispersity. Moreover, the increase in the degree of crystallinity during degradation affords an understanding of the observed macroscopic changes of the studied samples. The high crystallinity of the samples after biodegradation in compost explains their ability to fragment. Mechanical tests could be carried out for materials with lower crystallinity, i.e., biodegraded in soil and aged by artificial weathering.

Peer-reviewed version available at *Polymers* **2018**, *10*, 251; doi:10.3390/polym10030251

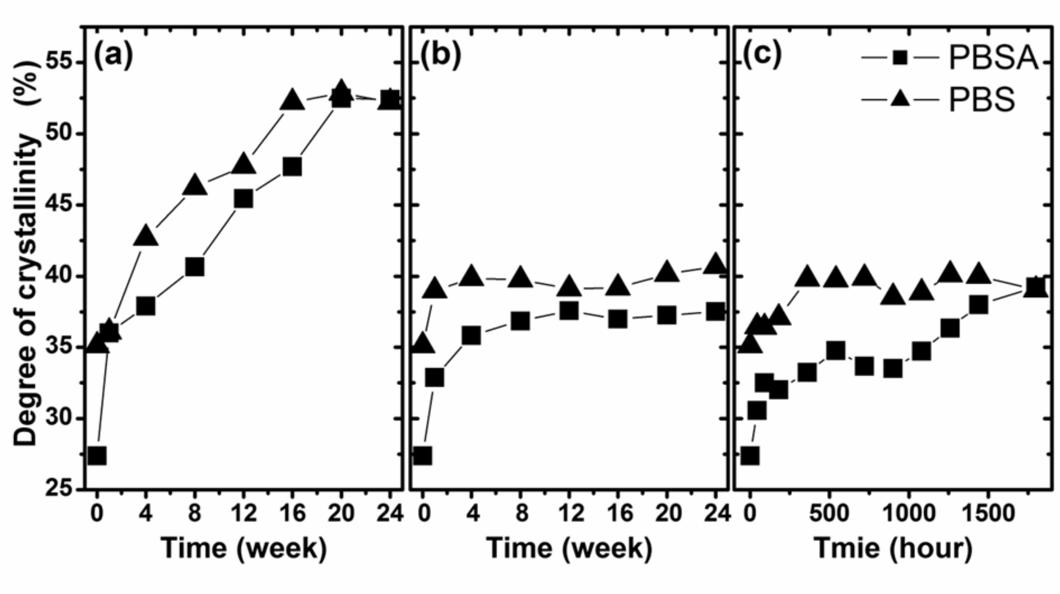

Figure 6. Changes in the crystallinity of the studied samples during degradation in selected environments: (**a**) biodegradation in compost, (**b**) biodegradation in soil and (**c**) artificial weathering.

Another characteristic feature of the structure of the studied polymers degraded under different conditions is the lattice length (d-spacing), which can be calculated according to Braggs equation (2):

$$d = \frac{\lambda}{2\sin\theta} \qquad (2)$$

where λ is the wavelength of the X-ray source (0,15418 nm) and θ is the angle of reflection (half of 2θ of the peak position). The d-spacing was calculated for the three most intense diffraction peaks, corresponding to the $(11\bar{1})/(002)$, (012) and (110) planes. In Figure 7, the change in the d-spacing of both studied polymers as a function of degradation time under various conditions is presented. As is presented, the most visible change in this structural parameter was observed during the initial period of degradation. The calculated d-spacing for the most intense diffraction peaks increased over up to 4 weeks of biodegradation in soil and in compost and up to 500 hours of artificial weathering. A longer degradation time caused a decrease in this parameter, and the most visible changes are observed for samples degraded by artificial weathering. The presented results suggest the ordering of the crystalline structures during degradation, which corresponds to the results of the molecular parameter changes as well as the macroscopic changes observed in the materials e.g., strain and elongation of the sample.

Peer-reviewed version available at Polymers 2018, 10, 251; doi:10.3390/polym10030251

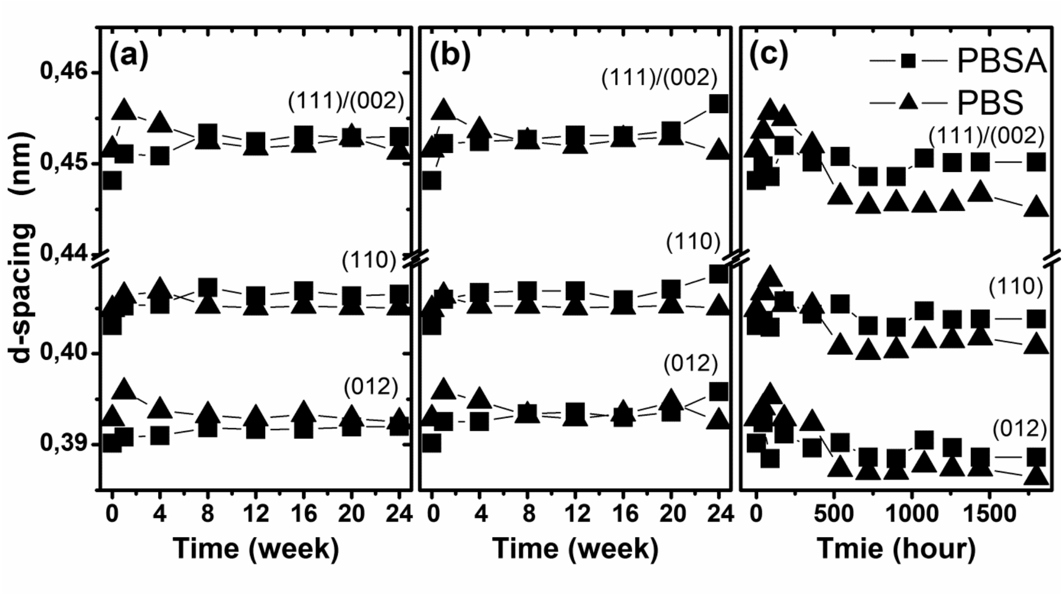

Figure 7. Changes in the d-spacing of the studied samples during degradation in selected environments: (a) biodegradation in compost, (b) biodegradation in soil and (c) artificial weathering.

4. Conclusions

The performed investigations on the degradation of commercially available PBS and PBSA copolymer in various environments affords a better understanding the changes in the polymers not only on the macroscale but also on the molecular and supramolecular scales. The results of the macroscopic measurements confirmed the better degradability of the PBSA copolymer compared with the PBS homopolymer. The most favorable degradation environment was compost, which contains microorganisms and natural enzymes that support degradation.

The analysis of the molecular parameters and supramolecular structures of both polymers during degradation showed that more significant changes occurred for PBS. All of the applied environments resulted in a decrease in the molar mass and an increase in the crystallinity of both polymers, but larger changes were recorded for PBS.

The analysis of the dispersity showed that each of the selected environments involved a different mechanism for the molecular changes and degradation. In the case of artificial weathering, the degradation of the polymer chains is random, and the dispersity increases with decreasing molar mass. The obviously different mechanism of chain decomposition is observed during biodegradation in compost, where the relatively slow hydrolysis of higher molar mass polymers and faster enzymatic etching of oligomers was observed by the decrease in molar mass with decreasing dispersity. Different results were recorded during degradation in soil, where only the molar mass was changed without changes in the dispersity.

The investigation of the supramolecular changes clearly showed the ordering of polymeric chains during degradation, as measured by the d-spacing. The most visible ordering was observed for the samples degraded by artificial weathering. In this case, the changes were more visible in PBS than the PBSA copolymer.

The experiment showed that, despite the larger macroscopic changes of the PBSA copolymer, larger molecular and supramolecular changes occurred in the PBS homopolymer.

Acknowledgments: This work was partially financed by European Regional Development Fund in the frame of “Biodegradable fibrous products” project (acronym BIOGRATEX) No. POIG 01.03.01-00-07/08-09. Part of work was financed from funds assigned for 14-148-1-2117 statuary activity by Lodz University of Technology, Department of Material and Commodity Sciences and Textile Metrology, Poland.

Author Contributions: Michał Puchalski performed the WAXD measurement, analysed all experimental data and wrote the paper; Grzegorz Szparaga performed the samples and the mechanical measurments; Tadeusz Biela performed the SEC-MALLS measurement and analysis; Sławomir Sztajnowski performed the laboratory artificial weathering of samples according to the ISO standards; Agnieszka Gutowska performed the

Peer-reviewed version available at *Polymers* **2018**, *10*, 251; doi:10.3390/polym10030251

laboratory biodegradation of samples in soil and compost according to the ISO standards; Izabella Krucińska designed experiment, the leader of Biogratex Project.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. Tokiwa, Y.; Calabia, B.P.; Ugwu, C.U.; Aiba, S. Biodegradability of Plastics. *Int. J. Mol. Sci.* **2009**, 10, 3722-3742, DOI. 10.3390/ijms10093722.
2. Mochizuki, M. Properties and Application of Aliphatic Polyester Products. *Biopolym. Online.* **2005**, 4. DOI. 10.1002/3527600035.
3. Xu, J.; Guo, B.H. Microbial Succinic Acid, Its Polymer Poly(butylene succinate), and Applications. In *Plastics from Bacteria. Microbiology Monographs*, Chen, G.Q. Springer: Berlin, 2010; 14, pp. 347-388, ISBN 978-3-642-03286-8.
4. Jacquel, N.; Freyermouth, F.; Fenouillot, F.; Rousseau, A.; Pascault, J.P.; Fuertes, P.; Saint-Loup, R. Synthesis and properties of poly(butylene succinate): Efficiency of different transesterification catalysts. *J. Polym. Sci. A Polym. Chem.* **2011**, 49, 5301–5312. DOI. 10.1002/pola.25009.
5. Nikolic, M.S.; Djonlagic, S. Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s. *Polym. Degrad. Stab.* **2001**, 74, 263–270, DOI. 10.1016/S0141-3910(01)00156-2.
6. Fujimaki, T. Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. *Polym. Degrad. Stab.* **1998**, 59, 209 – 214., DOI. 10.1016/S0141-3910(97)00220-6.
7. Ichikawa, Y.; Mizukoshi, T. Bionolle (Polybutylenesuccinate). In (eds) Synthetic Biodegradable Polymers. Advances in Polymer Science, Rieger, B.; Künkel, A.; Coates, G.; Reichardt, R.; Dinjus, E.; Zevaco, T. vol Springer: Berlin, 2011; 245, pp. 285-313, ISBN. 978-3-642-27153-3.
8. http://www.showa-denko.com/news/bionolle-the-pioneer-in-biodegradable (accessed on 20 01 2018)
9. McKinlay, J.B.; Vieille, C.; Zeikus, J.G.; Prospects for a bio-based succinate industry. *Appl. Microbiol. Biotechnol.* **2007**, 76, 727–740, DOI. 10.1007/s00253-007-1057-y
10. Bechthold, I.; Bretz, K.; Kabasci, S.; Kopitzky, R.; Springer, A. Succinic Acid: A New Platform Chemical for Biobased Polymers from Renewable Resources. *Chem. Eng. Technol.* **2008**, 31, 647–654, DOI. 10.1002/ceat.200800063
11. Debuissy, T.; Pollet, E.; Avérous, L.; Synthesis of potentially biobased copolyesters based on adipic acid and butanediols: Kinetic study between 1,4- and 2,3-butanediol and their influence on crystallization and thermal properties, *Polymer*, **2016**, 99, 204-213, DOI. 10.1016/j.polymer.2016.07.022.
12. Lichocik, M.; Owczarek, M.; Miros, P.; Guzińska, K.; Gutowska, A.; Ciechańska, D.; Krucińska, I.; Siwek, P. Impact of PBSA (Bionolle) Biodegradation Products on the Soil Microbiological Structure. *Fib. Text. East. Eur.* **2012**, 20, 179-185.
13. Siwek, P.; Libik, A.; Kalisz, A.; Zawiska, I. The effect of biodegradable nonwoven direct covers on yield and quality of winter leek. *Folia Hort.* **2013**, 25 61-65.
14. Bhatia, A.; Gupta, R.; Bhattacharya, S.; Choi, H. Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application. *Korea-Australia Rheol. J.*, **2013**, 19, 125-131.
15. Jompang, L.; Thumsorn, S.; On, J.W.; Surin, P.; Apawet, C.; Chaichalermwong, T.; Kaabbuathong, N.; O-Charoen, N.; Srisawat, N. Poly(lactic acid) and Poly(butylene succinate) Blend Fibers Prepared by Melt Spinning Technique. *Energy Procedia* **2013**, 34, 493 – 499, DOI. 10.1016/j.egypro.2013.06.777.
16. Krystyna Twarowska-Schmidt, Wacław Tomaszewski, Evaluation of the Suitability of Selected Aliphatic Polyester Blends for Biodegradable Fibrous Materials with Improved Elasticity. *Fib. Text. East. Eur.* **2008**, 16, 9–13.
17. Xu, J.; Guo, B.-H. Poly(butylene succinate) and its copolymers: Research, development and industrialization. *Biotechnol. J.* **2010**, 5, 1149–1163. DOI. 10.1002/biot.201000136
18. Lai, S.-M.; Huang, C.-K.; Shen, H.-F. Preparation and properties of biodegradable poly(butylene succinate)/starch blends. *J. Appl. Polym. Sci.* **2005**, 97, 257–264, DOI. 10.1002/app.21679.
19. Salehiyan, R.; Ray, S.S.; Bandyopadhyay, J.; Ojijo, V. The Distribution of Nanoclay Particles at the Interface and Their Influence on the Microstructure Development and Rheological Properties of Reactively Processed Biodegradable Polylactide/Poly(butylene succinate) Blend Nanocomposites. *Polymers* **2017**, 9, 350, DOI. 10.3390/polym9080350.
20. Gigli, M.; Negroni, A.; Zanaroli, G.; Lotti, N.; Fava, F.; Munari, A.; Environmentally friendly PBS-based copolyesters containing PEG-like subunit: Effect of block length on solid-state properties and enzymatic degradation. *React. Funct.. Polym.* **2013**, 73, 764–771 DOI. 10.1016/j.reactfunctpolym.2013.03.007.

Peer-reviewed version available at *Polymers* **2018**, *10*, 251; doi:10.3390/polym10030251

21. Tokiwa, Y.; Calabia, B.P. Biodegradability and Biodegradation of Polyesters. *J. Polym. Environ.* **2007**, 15, 259–267, DOI. 10.1007/s10924-007-0066-3.
22. Bautista, M.; de Ilarduya, A.M.; Alla, A.; Muñoz-Guerra, S. Poly(butylene succinate) Ionomers with Enhanced Hydrodegradability, Polymers **2015**, 7, 1232-1247, DOI. 10.3390/polym7071232
23. Ding, M.; Zhang, M.; Yang, J.; Qiu, J.-H. Study on the Enzymatic Degradation of Aliphatic Polyester–PBS and Its Copolymers. *J. Appl. Polym. Sci.* **2012**, 124, 2902–2907, DOI. 10.1002/app.35347
24. Kimble, L.D.; Bhattacharyya, D. In Vitro Degradation Effects on Strength, Stiffness, and Creep of PLLA/PBS: A Potential Stent Material. *Int. J. Polym. Mater. Polym. Biomater.* **2015**, 64, 299-310, DOI: 10.1080/00914037.2014.945203
25. Shih, Y.-F. Thermal Degradation and Kinetic Analysis of Biodegradable PBS/Multiwalled Carbon Nanotube Nanocomposites. *J. Polym. Sci. B.* **2009**, 47, 1231–1239, DOI. 10.1002/polb.21728.
26. Cho, K.; Lee, J.; Kwon, K. Hydrolytic Degradation Behavior of Poly(butylene succinate)s with Different Crystalline Morphologies, J. Appl. Polym. Sci. **2001**, 79, 1025–1033, DOI. 10.1002/1097-4628(20010207)79:6<1025::AID-APP50>3.0.CO;2-7.
27. Puchalski, M.; Siwek, P.; Biela, T.; Sztajnowski, S.; Chrzanowski, M.; Kowalska, S.; Krucińska, I. Influence of the homehold composting conditions on the structural changes of polylactide spun-bonded nonwovens during degradation. *Text. Res. J.* **2017**, 87, 2541-2549, DOI. 10.1177/0040517516673332.
28. Gutowska, A.;, Jóźwicka, J.; Sobczak, S.; Tomaszewski, W.; Sulak, K.; Miros, P.; Owczarek, M.; Szalczyńska, M.; Ciechańska, D.;, Krucińska, I. In-Compost Biodegradation of PLA Nonwovens. Fib. Text. East. Eur. **2014**, 22, 99-106.
29. Rabiej, M. Application of the genetic algorithms and multi-objective optimisation to the resolution of X-Ray diffraction curves of semicrystalline polymers. *Fib. Text. East. Eur*. **2003**, 11, 83-87.
30. Stepto, R.F.T.; Gilbert, R.G.; Hess, M.; Jenkins, A.D.; Jones, R.G.; Kratochvíl, P. Dispersity in Polymer Science. *Pure Appl. Chem.* **2009**, 81, 351–353, DOI:10.1351/PAC-REC-08-05-02.