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Degradation of the Blends of Natural and Synthetic Copolyesters in Different Natural Environments

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Summary: The paper presents results of the biodegradation of the blends of natural and synthetic copolyesters in two different natural environments. Environmental degradation took place in compost with activated sludge at sewage farm and - for comparison - in the Baltic Sea in Gdynia Harbour. Degradation of these blends was monitored for 16 weeks in compost and for 6 weeks in sea water. The changes in macroscopic features of surface and the weight loss of the samples were measured during the performed experiment. The characteristic parameters of compost and sea water were also controlled during all incubation time and their influence on the rate of biodegradation is discussed. The results of this study revealed that the natural aliphatic copolyester i.e. 3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) and its blends with the synthetic aliphatic-aromatic copolyester of 1,4-butandiol with adipic and terephthalic acids degrade faster in compost than in sea water. The rate of the biodegradation process depends on the composition of blends and different abiotic parameters of compost and sea water.

Keywords: activated sludge; 1,4-butandiol/adipic acid/ terephthalic acid copolyester; composting; 3-hydroxybutyrate/3-hydroxyvalerate copolyester; sea water

Introduction

Recently, there is growing demand of biodegradable polymers. They have acquired an important place in modern life. Products from biodegradable polymers have been implemented in the medical field, pharmacy, gardening, agriculture and packaging. Selective use of biodegradable polymers in certain applications might help to reduce the environmental impact of plastic wastes. The development of biodegradable polymers in natural environments is the key to solving problems caused by plastic wastes. But environmental degradation can only occur in favourable environments, where the biodegradation is expected to happen.

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Aromatic polyesters such as poly(ethylene terephthalate) exhibit excellent material properties but proved to be almost resistant to microbial attack [1]. Among polymers, which undergo controlled biological degradation by microorganisms, aliphatic polyesters play a predominant role, due to their potentially hydrolyzable ester bonds. The aliphatic polyesters of bacterial origin, such as polyhydroxyalkanoates (PHA), have been drawing much attention as biodegradable substitutes of conventional non-degradable polymers. Polyhydroxyalkanoates are produced by a wide variety of microorganisms as intracellular carbon and energy storage [2, 3]. The class of PHA includes among others the microbially synthesized copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV). This copolymer is truly biodegradable and readily degraded by a wide range of bacteria, fungi and algae [4]. The applications of PHBV are wide ranging and extend to any area, including the disposable hygiene, agricultural and packaging markets. However, bacterial polyesters often lack of good thermal and mechanical properties that are important from the point of view of their processing.

To combine good material properties with biodegradability, a new group of copolyesters have been developed as biodegradable polymers. This group includes the aliphatic-aromatic copolyester of 1,4-butandiol with adipic and terephthalic acids. According to DIN V 54900 and ASTM D-5338-98 this polymer is biodegradable, not toxic and useful in composting process [5]. This material can be used for a number of applications and promises to be very competitive.

The aim of the present study is an examination of the biodegradation of natural and synthetic copolyesters as well as their blends under natural and weather depending conditions such as compost with activated sludge and sea water.

Experimental

Materials

Natural aliphatic copolyester of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV) (3HV content 12%, Mn = 336000, Mw/Mn = 2.8) was supplied by Aldrich.

Synthetic aliphatic-aromatic copolyester of 1,4-butandiol with adipic and terephtalic acids was kindly provided by BASF.

The binary PHBV/synthetic copolyester blends (containing 40 and 50 %-wt of PHBV, respectively) were prepared by casting from chloroform solution on glass plates at room temperature. Films with thickness of 0.08-0.15 mm were obtained.

All polymer samples were cut into 1.5 x 10 cm rectangles and left at room temperature and weighed with a precision balance.

Environment

The incubation of natural and synthetic copolyesters took place in two different environments: in the compost with activated sludge from sewage treatment plant and – for comparison - in the Baltic Sea water under natural weathering conditions.

The characteristic abiotic parameters of compost and sea water were also investigated and their influence on the rate of biodegradation is discussed.

Biodegradation in compost with activated sludge

The compost used in this work was formed with the sample of activated sludge from sewage treatment plant in Gdynia. The 1.5 x 2.0 x 1.0m (width, length and height) compost pile was prepared under natural conditions of sewage farm. It consisted of the activated sludge, burnt lime and straw. Burnt lime (0.45kg CaO/1kg dry mass of compost) was added to ravage phatogenic bacterium and parasites eggs, to de-acidify activated sludge and to convert active sludge to compost. The straw was added to maintain the higher temperature of the compost pile [7]. We can expect that in the compost pile prepared under natural conditions the kind of living microorganisms is dependent on the place of pile. There were conditions from aerobic (upper part of pile), microaerophilic (in the middle) and facultative anaerobic (at the bottom).

The polymer samples were put into a special basket and buried in the core of the compost pile.The incubation lasted 16 weeks.

The characteristic parameters of compost were measured during the degradation time and are presented in Tab.1.

Table 1. Characteristic parameters of activated sludge compost

Parameter	Month		
	July	August	October
Temperature [°C]	19.5	22.6	13.4
pH	5.6	5.1	5.0
Moisture content [%]	48.8	46.2	46.4
Activity of dehydrogenases [mol/mg d.m.]	0.0398	0.0331	0.0263

Biodegradation in the Baltic Sea

The incubation of natural and synthetic copolyesters also took place in the Baltic Sea. The blend samples were located in a special basket at 2 m deep under the surface of the Baltic Sea, near the ship of Polish Ship Salvage Company, in Gdynia Harbour. The incubation lasted 6 weeks.

The characteristic parameters of sea water environment according to the Institute of Meteorology and Water Management, Maritime Branch are presented in Table 2.

Table 2. Characteristic parameters of Baltic Sea

Parameter	Month	
	July	August
Temperature [°C]	16.9	20.3
pH	8.1	8.1
Salinity [ppt]	6.61	6.14
Cl content [g/kg]	3.66	3.40
Oxygen content [cm^3/dm^3]	6.65	5.82

Methods

Characterization of compost

Dry mass in compost was determined according to Polish Standard [8]. The samples of compost were dried at 105°C until constant weight. Average samples of approximately 10 g required drying for at least 24 hours. The moisture content was calculated from the percent of dry mass in compost.

Compost pH. To 50 g samples of the compost, 100 ml of distilled water was added. Samples were homogenized for 30 min, left aside for 1 hour; then the pH of the extract was measured using a Teleko model N 5172f pH-meter.

Activity of dehydrogenases was measured by a spectrophotometric method with TTC (triphenyltetrazolium chloride). This method is based on the dehydrogenation of glucose added to the compost and transfer of hydrogen to the colorless biologically active TTC, which is reduced to TF (TTCH2, red compound). The intensity of this color was measured by using "Specol" colorimeter (490 nm). This is the method for an estimation of the biochemical activity of microorganisms in the activated sludge by oxidation process of organic compounds [9, 10].

Investigation of blends

After incubation, the samples were taken out from the test environments and washed with distilled water and dried at room temperature to constant weight. The macroscopic features of blend samples and changes of their weight were recorded during the degradation experiment.

The weight changes (%) were determined by a Gibertini E 42s electronic balance. The results obtained for clean and dried samples of blends after biodegradation experiments were compared with those of the respective samples before biodegradation. The weight loss was calculated, averaged over three specimens and expressed in percentage (%).

Results and Discussion

The abiotic parameters of compost (temperature, pH, and moisture content) and sea water (temperature, pH, salinity and oxygen content) had a significant influence on development of living microorganisms in natural environments.

The characteristic parameters of compost presented in Table 1 indicate that the average temperature of compost (~18.5°C) during composting was lower than that preferred for enzymatic degradation [11]. The pH values in both months were similar and the average pH in compost with activated sludge was acidic (5.5).

The low temperature and acidic pH of compost in our experiment stimulated the growth of psychrotrophic acidophilic microorganisms (mould), which therefore played the main role in the biodegradation experiment [12].

The activity of dehydrogenases depends on the degree of growth of microbial populations, capable to produce enzymes involved in the biodegradation process. During the experiment the activity of dehydrogenases in compost was observed to decrease (Table 1). With decreasing of moisture content the lower absolute value of activity of dehydrogenases was observed. Taking into consideration the characteristic of the compost it can be suggested that at the end of the composting process microaerophilic conditions, resulting from an activity of living organisms, were predominant, thus negatively affecting the activity of dehydrogenase.

The characteristic parameters of sea water in natural environment presented in Table 2 indicate that the average temperature (~18.6°C) of the Baltic Sea water was slightly lower such that that preferred for enzymatic degradation, whose optimal temperature is in the range of 20-60°C [11]. The value of pH in sea water was alkaline (8.1) during all the degradation experiment.

The low temperature of the Baltic Sea, as well as the slight alkalinity of water induced the growth of psychrotrophic bacteria. In the first period of incubation (July) the lowest temperature and the highest oxygen content were observed. These conditions have an influence on the activity of oxidizing enzymes. The situation was also favorable for the development of aerobic epilithic bacteria. The metabolism of these microorganisms probably caused the change of the concentration of carbon dioxide in sea water, thus decreasing the oxygen content at the end of the test (August-5.82 cm^3/dm^3. However, no significant pH change of sea water was observed [13].

The comparison of the characteristic parameters of compost and sea water, presented in Table 1 and 2, indicates that the temperature in both environments was almost at the same level and was lower than that preferred for enzymatic degradation [11]. However, the pH values were different and the average pH in see water was alkaline (8.1) while that of active sludge was slightly acidic (5.5).

The results of the weight changes of the polymer samples studied during biodegradation in compost and sea water are presented in Table 3 and 4 respectively.

The weight changes of the polymer samples indicate that natural aliphatic copolyester degrades in natural environments very fast. Biodegradation process of PHBV was faster in compost (the highest weight losses) than in seawater.

Table 3. The weight losses of polymer samples after biodegradation in compost with active sludge

Entry No.	Polymer Sample	Time [weeks]/weight loss [%]							
		2	3	4	5	6	8	10	16
1.	natural PHBV	22.8	70.6	91.3	disintegration				
2.	synthetic copolyester	1.6	-	2.0	-	2.1	3.2	4.9	30.6
3.	60%PHBV/40% synthetic copolyester	9.9	-	26.9	-	43.5	disintegration		
4.	50%PHBV/50% synthetic copolyester	4.1	-	4.3	-	16.9	53.4	disintegration	

Table 4. The weight losses of polymer samples after biodegradation in sea water

Entry No.	Polymer Sample	Time [weeks]/weight loss [%]			
		2	4	6	
1.	natural PHBV	6.4	20.1	54.0	the experiment is still continued
2.	synthetic copolyester	0.7	0.3	0.6	
3.	60%PHBV/40% synthetic copolyester	3.1	9.5	17.9	
4.	50%PHBV/50% synthetic copolyester	3.6	8.5	11.8	

After 5 weeks of incubation in compost all PHBV samples were disintegrated. For comparison, only approximately 54% of weight loss was noticed in sea water after 6 weeks incubation.

Disintegration in compost means fragmentation and loss of visibility of sample in the environment. However, biological degradation in the compost is supposed to be still continuing. Accordingly, in the composting process, the polymer sample degradation by macro and microorganisms and/or enzymes living in compost will proceed until they have been converted to carbon dioxide and water [14, 15].

The lowest degradation rate in compost and sea water was observed in the case of the synthetic aliphatic-aromatic copolyester. The composting process has lasted for 16 weeks (112 days), during this time frame ~30% weight loss was noticed. During all time of incubation in sea water no significant changes of weight (~1%) of synthetic aliphatic-aromatic copolyester specimens were observed.

According to DIN V 54900 and ASTM D-5338-98, polymers can to be classified as fully biodegradable when at least 60% of the total organic carbon of the polymeric material has been converted into carbon dioxide during a test interval of no longer than 180 days [5]. In these test methods, the synthetic aliphatic-aromatic copolyester investigated was mixed with compost and kept at 58°C, under aerobic conditions. Under these controlled composting conditions, it was ascertained that at least 60% of the total organic carbon of this type of copolyester was converted into carbon dioxide after 45 days [5].

The observed differences between the previously reported data and the current degradation test of the synthetic aliphatic-aromatic copolyester are most likely attributable to the dissimilarity of composting conditions. The characteristics parameters of the compost carried out under controlled conditions (humidity 42.5% and pH 7.16) were more favorable for biological degradation, whereas the opposite conditions occurred in the case of our experiment that was carried out under weather depending conditions (average temperature 18.5°C, pH 5.5, humidity 47.1%).

The exceptionally slow degradation process of synthetic aliphatic-aromatic copolyester observed in sea water degradation test in comparison to that observed in compost environment was probably caused by the different conditions of the Baltic Sea (temperature 18.6°C, pH 8.1), as well as by the different kind of microorganisms present in sea water.

The results presented in the Table 3 and 4 indicate that in both natural environments, binary blends consisting of natural and synthetic copolyesters degrade faster than the copolyester of 1,4-butandiol with adipic and terephtalic acids, but at a slower rate than the natural component PHBV. Generally, biodegradation process in compost is faster than in sea water.

Both blends were disintegrated in compost after 8 or 10 weeks. During all incubation time, the increase of the synthetic copolyester content in the binary blends caused a decrease of the degradation rate (the lower weight loss). The biodegradation process was less intensive in the case of blends containing 50%-wt of natural crystalline PHBV. After 6 weeks of incubation, the weight loss was almost twice lower than that of blends containing 60%-wt of natural crystalline PHBV. It means that the presence of the synthetic copolyester containing aromatic groups in blends is lowering the enzymatic degradation with respect to natural PHBV.

The lowest degradation rate was observed for the blends incubated in sea water. After 6 weeks, the blends of the natural aliphatic copolyester with the synthetic aliphatic-aromatic copolyester lost only 17.9 or 11.8% of their weight. However, a similar trend was observed during the degradation of blend samples in sea water as compared with degradation in compost. Accordingly, the lower biodegradation was observed when the content of the synthetic copolyester in blends increased.

Conclusions

The results of the present study indicate that natural copolyester of 3-hydroxybutyrate and 3-hydroxyvalerate, as well as its blends with the synthetic copolyester of butylene glycol with adipic and terephthalic acids degraded both in activated sludge compost and in sea water environments. The rate of the biodegradation process depended on the nature of environment. Generally, natural and synthetic copolyesters and their blends degraded faster in compost than in sea water. The composition of the blends had a significant influence on the degradation process in both natural environments. Moreover, the presence of the synthetic copolyester in blends decreased the disintegradability of blends in both the environments.

[1] Muller R., Kleeberg I., Deckwer W., *J. Biotechnol.,* **2001**, 86(2), 87
[2] Byrom D., *Trends Biotechnol.,* **1987**, 5, 246
[3] Sudes K., Abe H., Doi Y., *Prog. Polym. Sci.,* **2000**, 25, 1503
[4] Hammond T., Liggat J. J., in: Degradable Polymers, Edited by Scott G. and Gilead D., Chapman & Hall, London **1995**, p. 88-111
[5] Witt U., Proceedings of 7th Conference Biodegradable Polymers 2000, Wurzburg **2000**, pp. I1-I15
[6] Rutkowska M., Krasowska K., Heimowska A., Smiechowska M., Janik H., *Iranian Polym. J.,* **2000**, 9, 4, 221
[7] Siuta J., Wasiak G., *Ekologia i technika*, **1994**, 1, 20
[8] Polish Standard: BN-88/91103-07
[9] Polish Standard: PN-82/C-04616.08
[10] Hermanowicz W., Dojlido J, Dozanska W., Koziorowski B., Zerbe J., in: Fizyczno-chemiczne badanie wody i sciekow (Phisyco-chemical investigation of water and sludge), Arkady, W-wa **1999**, pp.498-499
[11] Lenz, W.R., Biodegradable polymers, In Advances in Polymer Science Vol. 107, Springer-Velay Berlin Heidelberg, 1993, pp. 1-40
[12] Rutkowska M., Krasowska K., Heimowska A., Kowalczuk M., in: Biorelated Polymers: Sustainable Polymer Science and Technology, E. Chiellini et. al., Ed., Kluwer Academic/Plenum Publishers, New York 2001, pp. 313 - 320
[13] Rutkowska M., Krasowska K., Heimowska A., Stelinka I., Janik H., Polym. Deg. Stab., 2002, in press
[14] Nayaran R., Mojo S., Summary of ASTM D6400-99 Test Methods and Specifications. Correlation of Test Methods to Real World, International Biodegradable Products Institute, 1999, pp. 3-9,
[15] Tuil R., Flower P., Lawther M., Weber C. J., in: Biobased Packaging Materials for the Food Industry, C. J. Weber, Ed., KVL Department of Dairy and Food Science, Frederiksberg, Denmark 2000, pp. 13-44