

Degradability of Different Packaging Polymeric Materials in Sea Water

Aleksandra Heimowska

*Department of Chemistry and Industrial Commodity Science
Faculty of Business Administration and Commodity Science
halex@am.gdynia.pl*

Katarzyna Krasowska

*Department of Chemistry and Industrial Commodity Science
Faculty of Business Administration and Commodity Science
kraska@am.gdynia.pl*

Maria Rutkowska

*Department of Chemistry and Industrial Commodity Science
Faculty of Business Administration and Commodity Science
rutmaria@am.gdynia.pl*

Abstract: The comparison of environmental degradability of different packaging polymeric materials in the Baltic Sea water was the subject of this paper. The experiment was also performed in laboratory at ambient temperature in a liquid medium containing sea water with sodium azide to evaluate the resistance of polymers against hydrolysis. The characteristic parameters of environment were measured during the period of degradation and their influence on degradation of polymers was discussed. The degradation processes of packaging polymers: polyethylene terephthalate, polyethylene, poly(ϵ -caprolactone), their modification with starch and natural poly(3-hydroxybutyrate-co-3-hydroxyvalerate) were studied by microscopic observations of polymer surfaces, changes of weight and tensile strength during the incubation under natural and laboratory conditions.

The obtained results confirm good resistance of pure polyethylene to sea water and indicate that the modification of polyethylene with starch improves degradability of this blend in natural aqueous biological environment.

Degradation of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(ϵ -caprolactone) in natural marine environment occurs very fast. And after 6 weeks incubation the poly(ϵ -caprolactone) samples were completely disintegrated.

Keywords: environmental degradation, sea water polyethylene, poly(ϵ -caprolactone), starch, polyethylene terephthalate, natural poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

1. INTRODUCTION

Several hundreds of thousands tons of plastics have been reported to be discarded into the marine environment every year. It has been estimated that one million marine animals are killed every year either by choking of floating plastic items or by becoming entangled in plastic debris. The development of biodegradable plastics is the key to solving the problems caused by marine plastic debris.

Sea water is a very complicated environment for degradation because microorganisms, animals, salt, sunlight, fluctuation of water, rain etc. all play a part in degradation in nature. The sea water is an example of environment where all kinds of micro- and macroorganisms, which could be involved in the degradation of polymers, are present.

According to the literature the first degradation step for nondegradable material such as polyethylene is oxidation. Photooxidation increases the amount of low molecular weight material by breaking bonds and increasing the surface area. In the second degradation step, microorganisms may utilize the abiotic degradation products and low molecular weight of polymer [1-2].

Biodegradation is the natural process in which the degradation of materials results from the action of naturally - occurring microorganisms such as bacteria, fungi or algae [3]. Biodegradable plastics break down completely into nonplastic and nontoxic constituents-substances like water, CO₂, CH₄ and biological materials [4].

Among degradable polymers poly(ϵ -caprolactone) is known as material susceptible to microbial degradation which could be a result of simple chemical hydrolysis of ester bonds or enzymatic attack or both [5-6].

The physical blending of degradable and nondegradable polymers with natural polymers such as starch is a way to prepare degradable polymers.

Starch is an inexpensive product available annually from corn and other crops. It is totally biodegradable in a wide variety of environments [7-9].

The aim of the present work was the comparison of the environmental degradability of packaging polymeric materials such as: polyethylene terephthalate, poly(ϵ -caprolactone) [10-12], polyethylene, their modification with starch [11,13] and natural poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [14] in the Baltic Sea water.

2. EXPERIMENTAL

2.1 Materials

The following materials has been studied and are presented:

- pure polyethylene terephthalate (PET) received from Melinex Process Research, Section ICI Polyester in Cliveland in England
- pure polyethylene (PE) received from "Petrochemia Plock S.A" in Poland,
- modified polyethylene containing 8% starch (PE/starch), received from "Starch and Potato Products Research Laboratory" in Poland,
- modified polyethylene containing pro-degradant additive in the form of a master batch (MB) in the amounts of 20% (PE+MB). The MB consisted mainly of corn starch, linear low-density polyethylene as the carrier resin, styrene-butadiene copolymer and manganese stearate; the last two are referred to as the pro-oxidant systems. The samples were prepared

in collaboration with EPRON Industries Ltd. and received from the Royal Institute of Technology in Stockholm, Sweden,

- pure poly(ϵ -caprolactone) (PCL) from Solvay, trademark CAPA 680 with reported MW=80.000,

- modified poly(ϵ -caprolactone) containing 60% (PCL/starch) from Novamont S.P.A. in Italy, trademark Mater-Bi Grade ZI01U made of starch and PCL,

- natural poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was supplied by Aldrich.

2.2 Environment

The environmental degradation of different packaging polymeric materials was carried out in the Baltic Sea water under natural weather depending conditions [10-16].

The incubation of polymer samples took place in the Baltic Sea water, in Gdynia Harbour. The samples were located in a special perforated basket at a depth of 2 meters in the sea.

The characteristic parameters of the Baltic Sea water such as: temperature, pH, salinity, oxygen content were monitored by The Institute of Meteorology and Water Management Maritime Branch in Gdynia, Poland (Tab. 1).

The experiment was also performed in laboratory in a liquid medium containing sea water with sodium azide ($\text{NaN}_3 \sim 0,195\text{g/l}$) to eliminate the influence of microorganisms on the degradation of the polymer samples. This experiment allowed evaluation of resistance of polymers to hydrolysis. Parameters of the Baltic sea water with NaN_3 are presented in Tab.2.

2.3 Investigation of polymer samples

After incubation the samples were taken out from environment and washed with distilled water and dried at room temperature to a constant weight.

The weight, surface morphology and mechanical properties of polymer samples were tested before and after degradation in environment.

2.3.1 The weight changes

The weight of polymer samples was estimated using Gibertini E 42s electronic balance. The percentage weight changes [%] were calculated from the weight data.

2.3.2 The tensile strength changes

The maximum tensile strength (MPa) was measured at room temperature using The Tensile Testing Machine Type Fu 1000e made by VEB Thuringer Industrierwerk Rauenstein, according to PN-EN ISO 527-1, 2, 3: 1998 Standard.

2.3.3 Microscopic observations

The surface of the of polymer samples was observed in micro scale (microscopic observation). Microscopic observations were analyzed with the optical microscope ALPHAPHOT-2YS2-H linked to a Nikon F90X camera at magnification 1:270. The surface was analyzed before and after biodegradation.

The changes in the whole samples of the polymer blends were performed with the optical transmission microscope „Boetius”, equipped with a polarizer, at a magnification of 1:250.

The pictures were taken before and after degradation.

3. RESULTS AND DISCUSSION

3.1 Characterization of environment

The characteristic parameters of sea water in natural environment presented in Tab. 1 indicate that the temperature of the Baltic Sea water was lower than that preferred for enzymatic degradation which is in the range of 20-60°C [17].

Table. 1 The characteristic parameters of the Baltic Sea water

Parameter	Month							
	Aug	Nov	Feb	Jun	Jul	Aug	Nov	Apr
Temperature [°C]	21,6	7,9	5,6	17,6	20,3	19,3	8,6	3,2
pH	8,5	8,3	8,2	8,5	8,2	8,9	8,1	-
Cl content [g/kg]	3,2	3,9	4,0	2,9	3,3	3,2	4,0	4,0
Oxygen content [cm ³ /dm ³]	7,5	8,3	10,8	7,5	7,6	7,4	6,4	-
Salt content [ppt]	5,8	7,0	7,3	5,4	5,6	6,0	7,2	7,3

Table. 2 The parameters of the sea water with NaN₃

Parameter	Month					
	Apr	Jun	Jul	Aug	Nov	Apr
Temperature [°C]	20	22	21	19	19	20
pH	7,8	7,1	7,8	7,6	6,8	7,9

In laboratory, the temperature was stabilized at a higher level (~20°C). The pH values were similar in both environments. The average pH was alkaline (8,2) in the sea water in the natural environment and 7,8 in the laboratory test, which is appropriate for enzymatic degradation (pH 5-8) [17]. The rather low temperature and slight alkalinity of Baltic Sea water had an influence on development of psychotropic and mesophilic bacteria.

The salinity and Cl content are higher in winter months than in summer months, but oxygen content is from 7,4-10,8 cm³/dm³.

The variety of micro- and macroorganisms in south Baltic Sea water and abiotic parameters (temperature, salinity) have an influence on microbiological activity of marine environment and consequently on degradation process of polymer samples.

3.2 The changes in polymeric materials during environmental degradation

The results of weight changes of polymer samples after incubation in Baltic Sea water are presented in Fig.1.

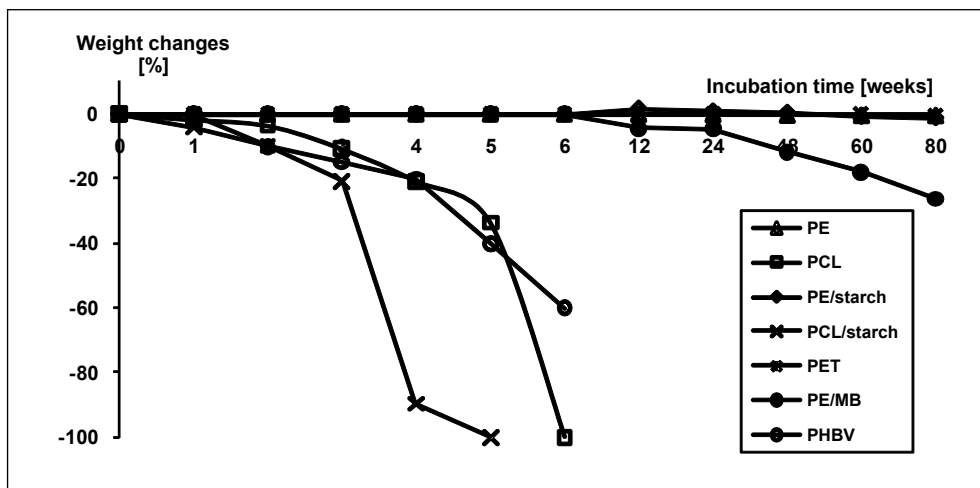


Figure. 1 Weight changes of polymer samples after incubation in the Baltic Sea water

Looking at the results we can observe that pure PET is the most resistant to sea water because we have not noticed any changes for 48 weeks of incubation in natural environment. This is because PET is aromatic polyester which is not susceptible for biodegradation.

There were no visible weight changes of pure PE. The degradation of polyethylene should be attributed primarily to photodegradation [1-2]. Low amount of solar radiation reaching the film under water surface can be one of the factors responsible for the low extent of oxidation process of PE.

We could expect the degradation process should be speeded up through microbiological consumption of the starch particles, producing a greater surface/volume ratio of the PE matrix.

It has been demonstrated that polyethylene with 8% starch is also not very susceptible to microbial degradation in sea water in natural environment, although it has been known that starch is readily degraded by a wide variety of yeast, fungi and bacteria. The samples PE/starch were even swollen at the beginning of the experiment (August-November) up to 1%, because starch was reversibly swollen [18].

The small weight losses were observed for the system with pro-oxidant (polyethylene with MB) in the first period of experiment (August-February). Then the degradation process speeded up. The starch removal was much greater from films containing the pro-oxidant components than from those without them. The degradation of polyethylene with MB is due to hydroperoxide - catalyzed autooxidation of the prooxidant in synergistic combination with biodegradation of the starch particles. Because of the synergistic process, the loss weight was much higher than the amount of the starch in added MB [18].

Analysis of the results shows that the temperature of the sea water has an influence on the rate of degradation. During winter (November-February) no weight loss was observed for blends of PE/starch.

At the first week (June) of incubation of natural PHBV, PCL and PCL/starch in Baltic Sea water small changes of weight were observed because of the low temperature for biodegradation process (17,6°C). In the next few weeks (July-August) the weight changes were much higher and after 5-6 weeks the sample of natural PHBV lost 60% of weight, but

both PCL samples were completely assimilated. The additive of starch speeded up a deterioration of PCL samples.

The results of weight changes of the polymer samples after incubation in sea water with NaN_3 are presented in Fig.2.

The weight changes of the samples incubated in sea water with NaN_3 were not significant, however, the temperature was higher than in the Baltic Sea.

The weight losses of pure PET, PE and PE/starch were lower than 0,6% after 48 weeks. The sterile samples show an overall slower autooxidation rate. The addition of sodium azide to keep the samples sterile might also interfere with the autooxidation.

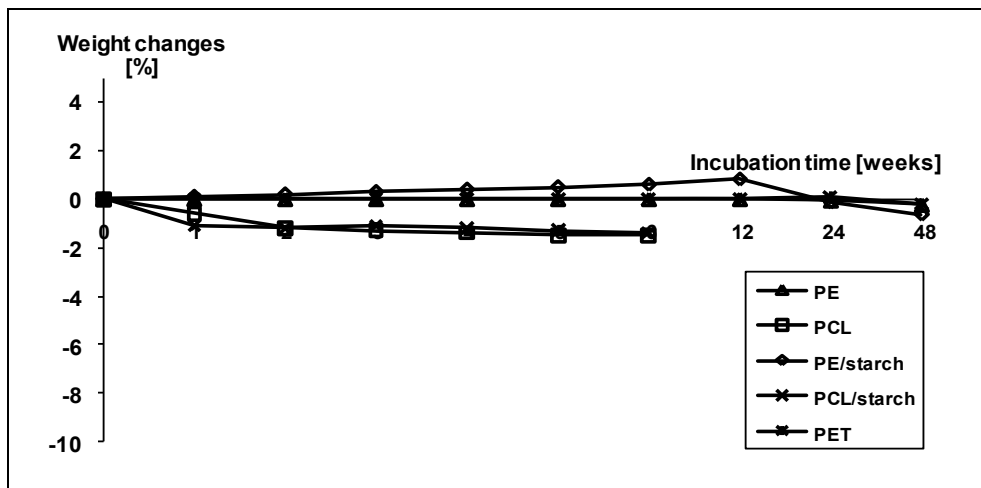


Figure. 2 Weight changes of polymer samples after incubation in the sea water with NaN_3

Azide compounds are known to undergo several reactions such as 1,3-dipolar addition to double bonds [19] or reaction with carboxylic acid [20]. The small weight changes were observed for PE/starch. At the beginning of the experiment (till 12 weeks) this sample was very little swollen (~1%). This swollen degree was comparable with results for PE/starch sample in the Baltic Sea water in natural environment. With the time of incubation small weight losses were noted. This is because starch was reversibly swollen at first up to a certain point (~1%) and after that the swelling become irreversible causing disruption of granules [18]. However the process was responsible for weight loss not more than 0,6%. The obtained results confirm that these packaging polymeric materials are resistant to the chemical hydrolysis.

The weight losses of the pure PCL and PCL/starch samples incubated in sea water with sodium azide were not significant (~1,5%). These changes might be explained by nonenzymatic hydrolytic ester cleavage.

The tensile strength of polymer samples after incubation in the Baltic Sea water is presented in Fig. 3.

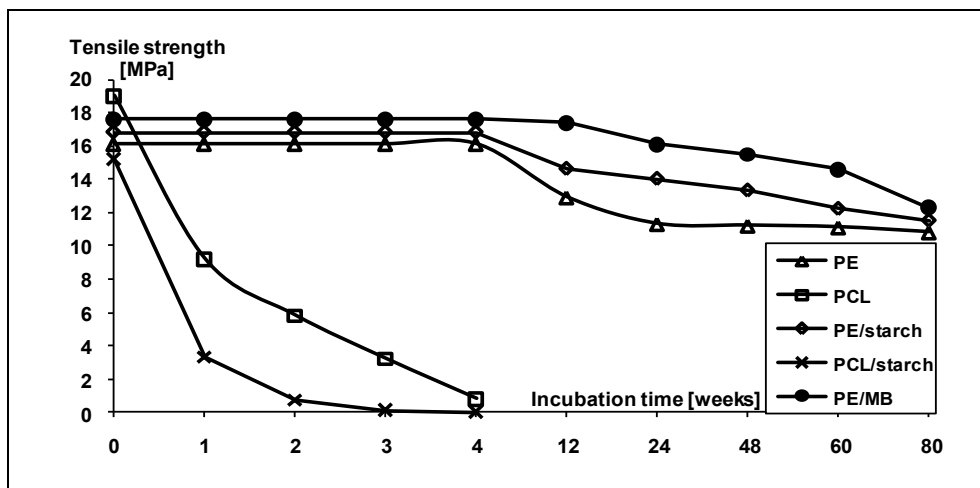


Figure. 3 The tensile strength of polymer samples after incubation in the Baltic Sea water

There were no special changes of tensile strength for PET during all incubation time (the tensile strength changed from 147MPa to 134MPa after incubation), what confirmed the results of weight changes.

There was no correlation between weight losses and tensile strength for PE samples but the changes of tensile strength after incubation in the Baltic Sea water were more visible than the changes of weight of pure PE, PE/starch and PE/MB. We can observed that the tensile strength decreases continuously for all PE samples incubated in the natural marine environment, which could be explained by some shear stresses (the fluctuation of water). Mechanical damage of the PE macrochains may be also caused by the swelling and bursting of growing cells of the invading microorganisms or by macroorganisms in sea water. Owing to mechanical damage of macrochains of PE, the value of the tensile strength of modified PE decreased about 30% although the weight decreased about 0,6%. We can also noticed no changes of weight for pure PE but the tensile strength decreased about ~30%.

The decrease of tensile strength of PCL and PCL/starch samples after incubation in sea water was observed explicitly and was associated with weight changes. The tensile strength was reduced as weight loss increased. The results of tensile strength confirmed faster biodegradation of PCL/starch, than pure PCL samples. During incubation of samples in the Baltic Sea water enzymatic degradation caused the surface erosion. Swelling and bursting of growing cells of the invading macro - and microorganisms might cause the mechanical damage to the surface of PCL. This was a reason of the dramatic decrease in tensile strength after incubation in the Baltic Sea water. The tensile strength of PCL samples incubated three weeks in sea water was very low ($\delta_B = 3$ MPa).

The tensile strength of polymer samples after incubation in the sea water with NaN_3 is presented in Fig. 4.

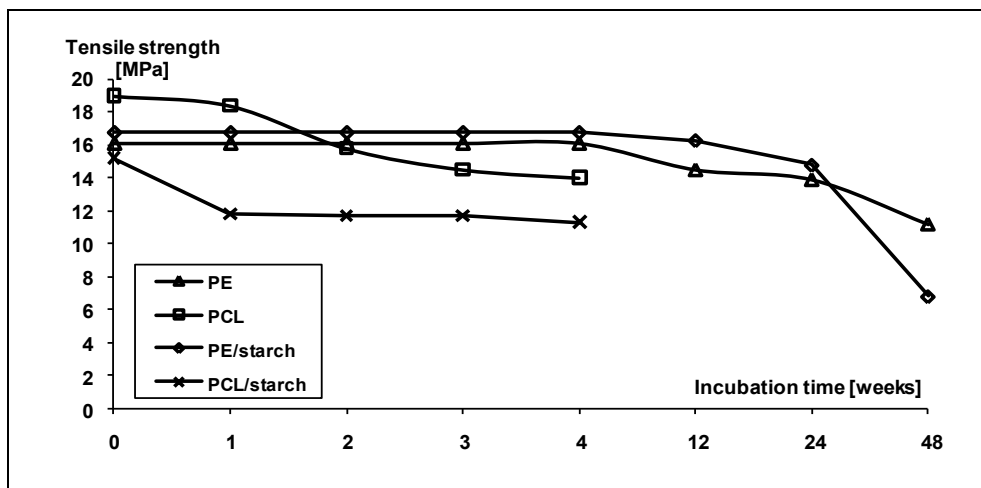


Figure. 4 The tensile strength of polymer samples after incubation in the sea water with NaN_3

Similar changes of tensile strength for all PE samples were observed during 24 weeks of incubation in the sea water with NaN_3 . Here, the changes of tensile strength of PE samples are more visible after 24 weeks of the experiment. For PE/starch after 48 weeks of incubation in sea water with NaN_3 the tensile strength decreased from 16,8 MPa to 6,8 MPa (when the changes in weight are not more than - 0,8% after the same time). The unusual change of tensile strength after 48 weeks of the experiment for PE/starch is probably caused by some release of starch (from the sample). Reduction of starch weakens polymer sample by creating wholes on the polymer surface after starch removal.

The results of tensile strength of both PCL samples after incubation in abiotic environment confirmed the results of weight changes. There were not visible changes in mechanical properties for PCL samples during all incubation time.

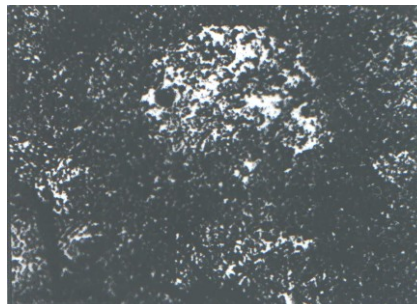
The degradation process of polymeric materials was described by changes in the morphology of the sample surface too.

There were no changes on photomicrographs surface of PET and PE samples during the all incubation time.

The microscopic observations of PCL samples are presented in Figure 5. After incubation in natural sea water the samples were not homogeneously destroyed and there were different images depending on where the picture was taken.



a) blank sample



b) after 2 weeks of degradation



c) after 4 weeks of



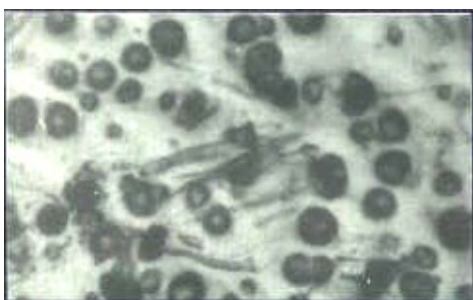
d) after 5 weeks of degradation

Figure 5. Photomicrographs surface of PCL sample under optical microscope at a magnification of 1:270 without polarisers, before and after incubation in sea water

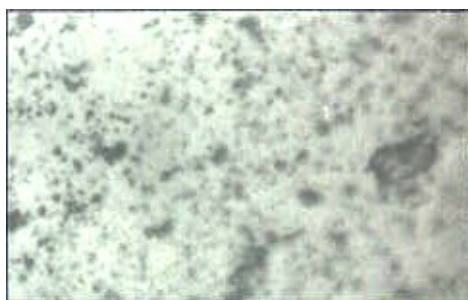
The surface of blank sample of PCL observed under optical microscope (Fig.5a) consisted of two phases (bright – crystalline and dark – amorphous). After 2 weeks of incubation in sea water we observed an increase of orientated birefringence elements which might be an evidence of an increase in crystallinity (Fig.5b). According to literature semicrystallinity of PCL plays a critical role in degradation phenomena, because the amorphous phase is degraded first and as a result an increase in crystallinity of polymers occurs, when most of the amorphous phase is degraded, subsequently the crystalline phase is degraded [21-23]. The microscopic observations could confirm that the amorphous phase was degraded first. After 4 weeks of experiment the decay of birefringent element was observed, crystalline phase began to degrade (less orientated birefringence elements) (Fig.5c). At the end of the experiment we could see very distinctly the black area on the surface of film studied, which represented an agglomeration of microorganisms (Fig.5d), and observation of PCL film morphology was unable to follow.

The surface of PE/MB after 24 weeks of incubation in sea water which is observed under the optical transmission microscope consisted still of the matrix (PE) and the dispersed phase (globules of starch). The image of starch globules were clearly destroyed after 80 weeks of incubation (Fig.6).

The microscopic observations are in agreement with the changes of weight and tensile strength of polyethylene with MB.



a) after 6 months incubation in sea water



b) after 20 months incubation in sea water

Figure 6. Microscopic structure of polyethylene with MB under the optical microscope „Boetius” at a magnification of 1:250 without polarizer

4. CONCLUSIONS

The obtained results confirmed good resistance of pure polyethylene and polyethylene terephthalate to sea water. Very little microbial degradation was observed for polyethylene/starch blend in the sea water, which was caused by low sea water temperatures, moderate biological activity of microorganisms and low amounts of solar radiation reaching the films. Globules of starch in modified polyethylene were destroyed first in marine environment. Then the oxidation process of polyethylene was speeded up because of a greater surface/volume ratio in the polyethylene matrix after removal of starch.

The degradation of polyethylene starch blends in sea water requires a long period of incubation and the special conditions of environment.

Biodegradation of natural poly(3-hydroxybutyrate-co-3-hydroxyvalerate), poly(ϵ -caprolactone) and poly(ϵ -caprolactone) with starch in sea water was very fast. The films of poly(ϵ -caprolactone) were completely assimilated over the period of 5-6 weeks. The obtained results indicate that poly(ϵ -caprolactone) was very sensitive to enzymatic attack of microorganisms in living environment and was rather resistant to chemical hydrolysis in abiotic environment. The addition of starch speeded up the deterioration of poly(ϵ -caprolactone) samples.

Biodegradation of poly(ϵ -caprolactone) in a microbially active environment occurred in two stages. The first stage consisted of the degradation of amorphous phase, resulting in an increase in crystallinity of the polymer. The second stage started when most of the amorphous regions were degraded. The polymer prone to fragmentation and enzymatic surface erosion proceeded.

REFERENCES

- [1] Falkiewicz-Dulik M., Janda K., Wypych G., "Handbook of Material Biodegradation, Biodeterioration and Biostabilization" ChemTec Publishing, Chap. 2, Toronto (2010)
- [2] ASTM Standards on Environmentally degradable Plastics, ASTM Publication Code Number (PCN): 1993, 003-420093-19
- [3] Singh B., Sharma N., "Mechanistic implications of plastic degradation" Polymer Degradation and Stability Vol 93, No 3, (2008), pp. 561-584
- [4] Gu J-D. "Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances" International Biodeterioration and Biodegradation Vol 52, No 2, (2003), pp. 69-91
- [5] Li S, Vert M., "Bioderagation of aliphatic polyesters" in "Dedradable Polymers"(eds G.Scott, D. Gileat), Chapman and Hall, Chap.4, London (1995)
- [6] Peng H., Ling J., Liu J., Zhu N., Ni X., Shen Z. "Controlled enzymatic degradation of poly(ϵ -caprolactone)-based copolymers in the presence of porcine pancreatic lipase" Polymer Degradation and Stability Vol 95, No 4, (2010), pp. 643-650
- [7] Imam S.H., Gordon S.H., Mohamed A., Harry-O'kuru R., Chiou B.-S., Glenn G.M., Orts W.J. "Enzyme catalysis of insoluble cornstarch granules: Impact on surface morphology, properties and biodegradability", Polymer Degradation and Stability, Vol. 91, No 12, (2006), pp. 2894-2900
- [8] Alvarez V.A., Ruseckaite R.A., Vázquez A." Degradation of sisal fibre/Mater Bi-Y biocomposites buried in soil" Polymer Degradation and Stability Vol 91, No 12, (2006), pp. 3156-3162

- [9] Gattin R., Copinet A., Bertrand C., Couturier Y. "Biodegradation study of a starch and poly(lactic acid) co-extruded material in liquid, composting and inert mineral media" *International Biodeterioration and Biodegradation* Vol 50, No 1, (2002), pp. 25-31
- [10] Krasowska K., Heimowska A., Rutkowska M., „Enzymatyczna degradacja poli(ϵ -kaprolaktonu) w warunkach naturalnych" *Polimery*, Vol 51, No 1, (2006), pp. 21-26
- [11] Rutkowska M., Krasowska K., Heimowska A., Steinka I., „Wpływ modyfikacji poli (ϵ -kaprolaktonu) na jego biodegradację w warunkach naturalnych" *Polimery*, Vol 47, No 4, (2002), pp. 36-42
- [12] Rutkowska M., Krasowska K., Heimowska A., Steinka I., Janik H., Haponiuk J., Karlsson S. "Biodegradation of modified poly(ϵ -caprolactone) in different environments" *Polish Journal of Environmental Studies*, Vol 11, No 4, (2002) pp. 413-420
- [13] Rutkowska M., Heimowska A., Krasowska K., Janik H., „Biodegradability of polyethylene starch blends in sea water" *Polish Journal of Environmental Studies*, Vol 11, No 3, (2001) pp. 267-274
- [14] Rutkowska M., Krasowska K., Heimowska A., Adamus G., Sobota M., Musioł M., Janeczek H., Sikorska W., Krzan A., Zagar E., Kowalczyk M., „Environmental degradation of blends of atactic poly[(R, S)-3 – hydroxybutyrate] with natural PHBV in Baltic Sea water and compost with activated sludge" *Journal of Polymer Environment*, Vol 16, (2008), pp. 183-191
- [15] Rutkowska M., Heimowska A., Krasowska K. "The influence of sea water on degradation of plastic packaging material", *Physicochemical problems of natural waters ecology*, H. Gurgul (red.), Wydawnictwo Naukowe Uniwersytetu Szczecińskiego, Vol III, pp. 255-268, Szczecin (2005)
- [16] Rutkowska M., Heimowska A. "Degradacja materiałów polimerowych pochodzenia naturalnego w środowisku wody morskiej", *Polimery* Vol 53, (2008) pp. 854-867
- [17] Lenz W. R., "Biodegradable Polymers, in *Advances in Polymer Science*", Vol 107, Springer-Verlag, pp. 1-40, Berlin, Heidelberg (1993)
- [18] Berenstedt C., PhD Thesis: "Environmental Degradation of Starch-modified Polyethylene: Degradation Products and Long-term Properties", Department of Polymer Technology, The Royal Institute of Technology, Stockholm (1994)
- [19] Sykes P., "A Guidebook to Mechanisms in Organic Chemistry", Longman Singapore Publishers, pp.194, Singapore (1986)
- [20] Sykes P., "A Guidebook to Mechanisms in Organic Chemistry", Longman Singapore Publishers, pp.123, Singapore (1986)
- [21] Jarrett P., Benedict C. V., Bell J. P., Cameron J. A., Huang S. J., "Polymers as Biomaterials" (eds S. W. Shalaby, A.S. Hoffman, B.D. Ratner and T.A. Horbett), Plenum Press, pp.181, New York (1991)
- [22] Bosworth L. A., Downes S. "Physicochemical characterisation of degrading polycaprolactone scaffolds" *Polymer Degradation and Stability* Vol 95, No 12, (2010), pp. 2269-2276
- [23] Agarwal S., Speyerer Ch. "Degradable blends of semi-crystalline and amorphous branched poly(caprolactone): Effect of microstructure on blend properties" *Polymer* Vol 51, No 5, (2010), pp. 1024-1032