

# Biodegradability of Polyethylene Starch Blends in Sea Water

M. Rutkowska<sup>1</sup>, A. Heimowska<sup>1</sup>, K. Krasowska<sup>1</sup>, H. Janik<sup>2</sup>

<sup>1</sup> Gdynia Maritime Academy, 83 Morska St., 81-225 Gdynia, Poland

<sup>2</sup> Technical University of Gdańsk, 80-952 Gdansk, Poland

*Received: 27 July, 2001*

*Accepted: 29 October, 2001*

## Abstract

The subject of this work is the degradation of pure polyethylene and modified polyethylene films containing 5% and 8% starch, and polyethylene with pro-degradant additives in the form of "master batch" in amounts of 20%.

The degradation of polymer samples was studied under marine exposure conditions in the Baltic Sea. The experiment was also performed in laboratory at the ambient temperature, in a liquid medium containing sea water with sodium azide ( $\text{NaN}_3$ ) to evaluate the resistance of polyethylene against hydrolysis. The incubation of polyethylene samples took 20 months. The characteristic parameters of environment were measured during the period of degradation and their influence on degradation of polyethylene was discussed. Changes in weight, tensile strength and morphology of polymer samples were tested during the experiment performed.

**Keywords:** polyethylene starch blends, sea water, environmental degradation

## Introduction

Several hundred thousand 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 on floating plastic items or by becoming entangled in plastic debris. The development of degradable plastics in nature is the key to solving the problems caused by marine plastic debris [1].

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 [2]. Biodegradable plastics break down completely into nonplastic and nontoxic constituent-substances like water,  $\text{CO}_2$ ,  $\text{CH}_4$  and biological materials.

It is known that biodegradation is not significant in the first step of biological degradation of polyethylene, which has a good resistance to microorganisms [3]. The oxidation is an important first degradation step for non-hydrolysable materials such as polyethylene. Photo-

oxidation 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 polymer [4].

Relatively inert polyethylene could become more degradable by introducing additives to it. Starch is used as a biodegradation additive [5]. Beside starch, the pro-oxidant formulation consisting of an unsaturated polymer, a transition-metal salt and thermal stabiliser, can also be used as additives for polyethylene [6]. The major role of starch has been found to provide higher oxygen permeability as it is consumed by microorganisms. The matrix is hollowed out and the surface/volume ratio increases. Another effect of the higher permeability of the matrix is the facilitated release of degradation products from the samples. This is most obvious when the degradation is performed in an aqueous environment [6].

Polyethylene starch blends are also susceptible to macrobiodegradation, degradation caused by organisms

larger than bacteria or fungi such as insects and larger animals [5]. The sea water is an example of an environment where all kinds of micro- and macroorganisms, which could be involved in the degradation of polymers, are present.

The aim of this paper is an examination of biodegradability of modified polyethylene in sea water.

## Experimental

### Materials

The following materials were studied:

- pure polyethylene (PE+0%) received from "Petrochemia Plock S.A" in Plock, Poland
- polyethylene containing 5% starch (PE+5%); received from "Starch and Potato Products Research Laboratory" in Poznan, Poland
- polyethylene containing 8% starch (PE+8%); received from "Starch and Potato Products Research Laboratory" in Poznan, Poland
- polyethylene with a 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 [6]. The samples were prepared in collaboration with EP-IRON Industries Ltd. and received from the Royal Institute of Technology in Stockholm, Sweden.

Polyethylene films were cut into 15 x 2 cm rectangles with 0.08 mm thickness. The samples were left at room temperature and weighed with a precision balance. Average weight of each polyethylene sample was 0.2 g.

### Environment

The incubation of polymer samples took place in the Baltic Sea water near a ship of the Polish Ship Salvage Company in Gdynia Harbor. The blend samples were located in a special basket (40 cm length, 40 cm width and 20 cm height; made from perforated sheet metal plate) at a depth of 2 meters in the sea.

The characteristic parameters of the Baltic Sea water were measured at The Institute of Meteorology and Water Management Maritime Branch and presented in Tab. 1.

The experiment was also performed in laboratory in a liquid medium containing sea water with sodium azide ( $\text{NaN}_3$  - 0.195 g/l) to eliminate the influence of microorganisms on the degradation of the polyethylene samples. This experiment allowed evaluation of resistance of polyethylene blends to hydrolysis. The incubation of polyethylene samples took 20 months.

Parameters of the sea water with  $\text{NaN}_3$  are presented in Tab. 2.

### Investigation of Polyethylene Samples

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

Table 1. The characteristic parameters of Baltic Sea water.

Parameter	Month					
	Aug (1 month)	Nov (3 months)	Feb (6 months)	July (12 months)	Nov (15 months)	Apr (20 months)
Temperature [°C]	21.6	7.9	5.6	19.3	8.6	3.2
pH	8.5	8.3	8.2	8.2	8.1	-
Cl content [g/kg]	3.2	3.9	4.0	3.3	4.0	4.0
Oxygen content [cm <sup>3</sup> /dm <sup>3</sup> ]	7.5	8.3	10.8	7.6	6.4	-
Salt content [ppt]	5.8	7.0	7.3	5.9	7.2	7.3

Table 2. The parameters of the sea water with  $\text{NaN}_3$ .

Parameter	Month			
	April (1 month)	July (3 months)	Nov (6 months)	April (12 months)
Temperature [°C]	20	21	19	20
pH	7.8	8.7	6.8	7.9

Changes in the weight, tensile strength and morphology of polyethylene blends were tested during the experiment.

- *The weight changes* [%] were determined using a Gibertini E42s electronic balance. The results obtained for clean and dried samples of polyethylene blends after degradation were compared with those of the respective samples before biodegradation. Average from 3-5 polyethylene samples was the final result of investigation.

- *Tensile strength* of polyethylene blends was measured on a Tensile Testing Machine according to the Polish Standards [8].

- *The changes on the surface* [9] of polymer blends were analyzed with an optical reflection microscope PZO (the so-called metallographic microscope) equipped with a polarizer and coupled to a computer by a CC20P Video TRONIC Int. GmbH camera. Final magnification was 1:300.

- *Changes in the whole samples* [9] of 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.

## Results and Discussion

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[7].

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

There were no visible weight changes of pure polyethylene. The degradation of polyethylene should be at-

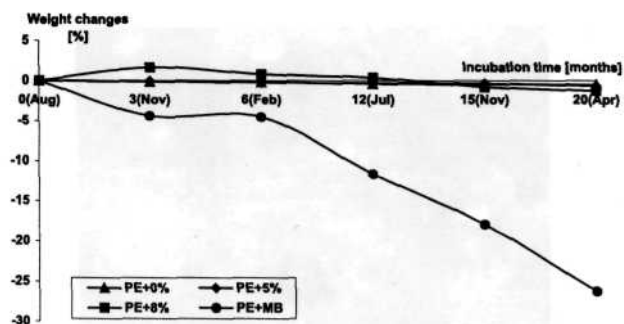


Fig. 1. Weight changes of polyethylene after incubation in the Baltic Sea water.

tributed primarily to photodegradation [6]. The low amount of solar radiation reaching the film under the surface might be one of the factors responsible for the low extent of oxidation process of polyethylene.

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

It has been demonstrated that polyethylene modified with starch (5 and 8%) is also not very susceptible to microbial degradation in the 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 with 8% starch were even swollen at the beginning of the experiment up to 1%, because starch was reversibly swollen [6].

The small weight losses were observed for the system with pro-oxidant (polyethylene with MB) in the first period of the experiment (August-February). Then the degradation process sped up. 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 weight loss was much higher than the amount of the starch in added MB [6].

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 polyethylene with starch and for polyethylene with a pro-degradant additive. Higher temperature in summer months has a visible influence on the weight loss of polyethylene with the MB additive. The degradation process in this period was considerable, and after 20 months weight loss of the samples reached 26%.

The results of weight changes of the polymer samples after incubation in the sea water with  $\text{NaN}_3$  are presented in Fig. 2.

In laboratory, the temperature was stabilized at a higher level ( $\sim 20^\circ\text{C}$ ). The pH values were similar in both environments. Average pH was alkaline (8.2) in sea water in the natural environment and 7.8 in the laboratory test, which is appropriate for enzymatic degradation (pH5-8)[7].

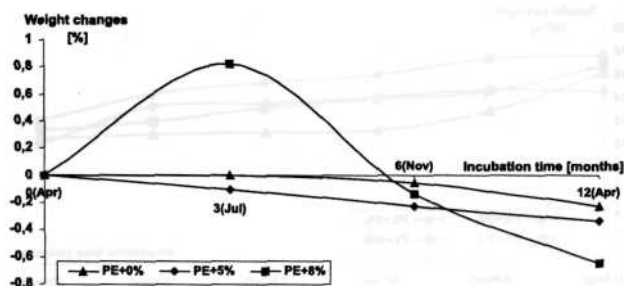


Fig. 2. Weight changes of polyethylene after incubation in the sea water with  $\text{NaN}_3$ .

The weight changes of the samples incubated in sea water with  $\text{NaN}_3$  were not significant; however, the temperature was higher than in the sea. The weight losses of pure polyethylene and polyethylene blends were lower than 0.6% after 12 months. The sterile samples show an overall slower autooxidation rate. The addition of sodium azide to keep the samples sterile may also interfere with autooxidation. Azide compounds are known to undergo several reactions such as 1,3-dipolar addition to double bonds [10] or reaction with carboxylic acid [11]. The highest weight changes were observed for polyethylene with 8% starch. At the beginning of the experiment this sample was very little swollen ( $\sim 1\%$ ). This swollen degree was comparable with results for PE+8% sample in Baltic Sea water in the 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 ( $\sim 1\%$ ) and after that the swelling became irreversible, causing a disruption of granules [6]. However, the process was responsible for weight loss of not more than 0.6%.

The obtained results confirm that these polyethylene blends are resistant to chemical hydrolysis.

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

There is no correlation between weight losses and tensile strength but the changes of tensile strength after incubation in the Baltic Sea water are more visible than changes of weight. We can observe that the tensile strength decreases continuously for all samples (including pure polyethylene) incubated in the natural marine environment, which could be explained by some shear stresses (the fluctuation of water). Mechanical damage to the polyethylene macrochains may be also caused by the swelling and bursting of growing cells of the invading microorganisms or by macroorganisms in the sea water. Owing to mechanical damage of macrochains of polyethylene, the value of the tensile strength of modified polyethylene decreased about 30% although the weight decreased about 0.6%. We can also notice no changes of weight for pure polyethylene but the tensile strength decreased about  $\sim 30\%$ .

The tensile strength of polymer samples after incubation in the sea water with  $\text{NaN}_3$  is presented in Fig. 4.

Similar changes of tensile strength for all samples were observed during 6 months of incubation in the sea water with  $\text{NaN}_3$ . Here, the changes of tensile strength of polyethylene samples are more visible after 6 months of

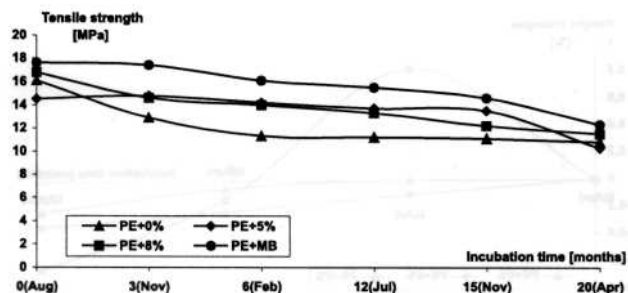


Fig. 3. The tensile strength of polyethylene after incubation in the Baltic Sea.

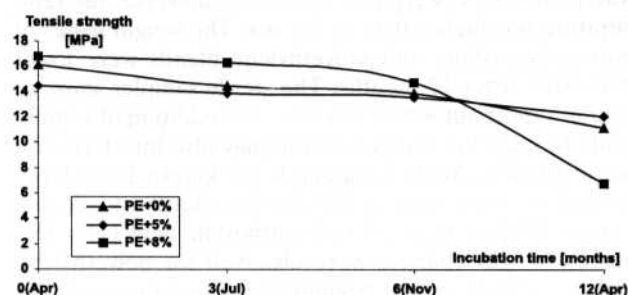


Fig. 4. The tensile strength of polyethylene after incubation in the sea water with  $\text{NaN}_3$ .

the experiment. For polyethylene with 8% starch additive, after 12 months of incubation in sea water with  $\text{NaN}_3$ , 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 12 months of the experiment for polyethylene with 8% starch additive is probably caused by some release of starch (from the sample). Reduction of starch weakens the polymer sample by creating holes on the polymer surface after starch removal.

An example of microscopic images of the samples studied (PE+MB) are presented in Figs. 5, 6. Generally, from microscopic observation we can conclude that after incubation in the natural environment, not every sample is destroyed homogeneously and that there are different images depending on the place of observation. However, some conclusions can be drawn.

The surface of blank samples of polyethylene with MB observed under metallographic microscope consists of the matrix and the dispersed phase. The polyethylene matrix is birefringent. Some globules of starch, as a dispersed phase in the matrix, are also birefringent but to a lesser degree than the matrix (Fig. 5a).

After six months of incubation of polyethylene with MB in sea water in the natural environment, the clear image of starch globules begins to fade out on the surface (Fig. 5b).

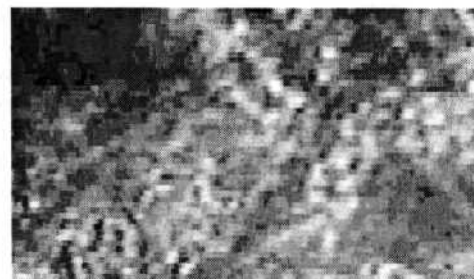
After 12 and 20 months of incubation the deterioration process of starch is more visible (Fig. 5c,d). At the end of the incubation time we can observe some dark



a) Blank



b) After 6 months incubation in sea water



c) After 12 months incubation in sea water



d) After 20 months incubation in sea water

Fig. 5. Microscopic surface of polyethylene with MB under the metallographic microscope at a magnification of 1:300 without polarizer.

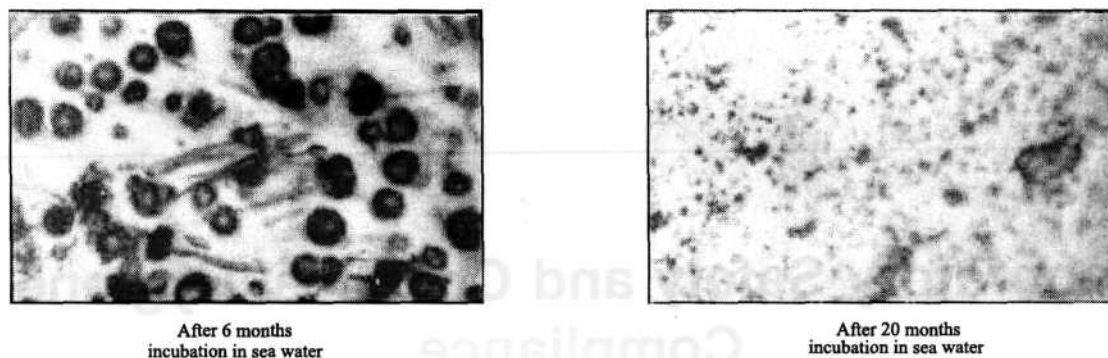


Fig. 6. Microscopic structure of polyethylene with MB under the optical microscope "Boetius" at a magnification of 1:250 without polarizer.

places. This observation could be explained by the presence of microorganisms (irregular black places) or the holes after starch removal (globular shape) on the surface of polymer blends.

The changes on polymer surface observed under metallographic microscope (Fig. 5) are different than the changes of the structure in the whole sample (Fig. 6a) performed with the optical transmission microscope "Boetius". Accordingly, after 6 months we can still observe clear globules of starch inside the polymer blend, which are clearly destroyed after 20 months (Fig. 6b). The microscopic observations are in agreement with the changes of weight and tensile strength of polyethylene with MB.

### Conclusion

In conclusion, very little microbial degradation was observed for polyethylene blends in the sea water, which was explained by low sea water temperatures, moderate biological activity of microorganisms and low amounts of solar radiation reaching the films. The degradation process of polyethylene blends in the natural environment depends on the quantity of starch in polyethylene blends and the conditions of the natural environment. Globules of starch in some modified polyethylene are destroyed first in marine environment, which weakens mechanical characteristics of polyethylene blends. Then the oxidation process of polyethylene is speeded up because of a greater surface/volume ratio in the polyethylene matrix after removal of starch.

The obtained results confirm good resistance of pure polyethylene to sea water and indicate that the introduction of pro-degradant additive into the polyethylene improves biodegradability of this blend in natural aqueous biological environment.

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

### References

1. DOI Y, KANESAWA Y., TANAHASHI N., KUMAGAI Y., Biodegradation of Microbial Polyesters in the Marine Environment, *Polymer Degradation and Stability*, 36, 173, **1992**.
2. ASTM Standards on Environmentally degradable Plastics, ASTM Publication Code Number (PCN): 1993, „003-420093-19 .
3. ALBERTSSON CH., ANDERSSON S. O., KARLSSON S., *Polymer Degradation and Stability*, **18**, 73, **1987**.
4. ALBERTSSON Ch., *J. Appl. Polym. Sci.* **22**, 3419, **1987**.
5. ALBERTSSON CH., Karlsson S., Conference Proceedings: Degradable Polymers for the Future, *Polymers from Renewable Resource and their Degradation*, Department of Polymer Technology, Stockholm, Sweden, **1994**.
6. 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, Sweden, **1994**.
7. LENZ W. R., Biodegradable Polymers, in *Advances in Polymer Science*, Vol. 107, Springer-Velay, Berlin, Heidelberg, pp. 1-40, **1993**.
8. Polish Standard PN-81/C-89034..
9. JANIK H., *Macromol. Symp.* **130**, 179, **1998**.
10. SYKES P., *A Guidebook to Mechanisms in Organic Chemistry*, Longman Singapore Publishers, Singapore, pp.194, **1986**
11. SYKES P., *A Guidebook to Mechanisms in Organic Chemistry*, Longman Singapore Publishers, Singapore, pp.123, **1986**.