Environmental degradability of polycaprolactone under natural conditions

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Abstract. The aim of this work was an estimation of susceptibility of biodegradable poly(ε-caprolactone) (PCL) to environmental degradation in different natural environments. The commercial poly(ε-caprolactone) film, the trade name "CAPA 680", was degraded in the compost, pond, open and harbour area of the Baltic Sea. Characteristic parameters of all natural environments were monitored during the incubation of polymer samples and their influence on degradation of PCL was discussed. Susceptibility of PCL to degradation in natural environments was evaluated based on changes of weight, crystallinity and polymer surface morphology. The rate of environmental degradation of PCL depended on the incubation place, environmental conditions and decreased in order: compost>harbour area of the Baltic Sea>open area of the Baltic Sea>pond.

1 Introduction

In recent decades world consumption of polymers has increased exponentially. Polymers are used in many areas, especially in the packaging, agriculture, medicine etc. In the process of consuming products humans generate plastic waste, which are responsible for the problem of environmental pollution. Nowadays, plastics which are not incinerated, landfilled or recycled are found in the nature and they polluting for example seas, rivers, oceans, lakes, beaches, forests etc. Very often the natural environment must serve as a waste repository, either by absorbing or recycling them into useful or at least harmless substances. When the waste products exceed the environment's ability to absorb them, the result is water, soil and air pollution.

The increase in volume of synthetic non-degradable polymers, particularly in the form of one-trip packaging, presented a potential threat to the natural environment. The plastic packaging litter is not only the aesthetically undesirable but it causes the possibility of risk for people, animals, birds on the land and in the water.

Recently the increasing attention is paid to attempt rational replacement commonly used synthetic polymers by biodegradable polymers. The use of biodegradable polymers in consumer products should not lead to the generation of toxic or otherwise environmentally unacceptable chemicals in the natural environment.

Biodegradable polymers are susceptible to biological degradation, resulting in the disintegration and mineralization under the action of living organisms. The initial breakdown of a polymer, which is the first step of biological degradation process can result from physical and biological forces, which can cause mechanical damage such as cracking of polymeric materials and fragmentation. Most polymers are too large to pass through cellular membranes, so they must be depolymerized to smaller molecules before they can be adsorbed and degraded within microbial cells. The monomers, dimers and oligomers of a polymer's repeating units are much easily degraded and mineralized, because they can be assimilated through the cellular membrane and then further degraded by cellular enzymes. Under oxygen conditions, aerobic microorganisms are mostly responsible for degradation of polymer. Biomass, carbon dioxide and water are the final products of deterioration. As opposite to this, under anoxic conditions, anaerobic microorganisms play the main role in polymer destruction. The primary products are methane, water and biomass [1, 2].

In the case of environmental degradation under natural conditions very often synergistic action various factors including temperature, pH, humidity, aeration, sunlight, macroorganisms, microorganisms and enzymes leads to degradation of biodegradable polymers.
Biodegradable polymers have been found to degrade more rapidly if a combination of microbes is used rather than one specific microbe. Thus the presence of large varieties of microbes in the natural environment support faster biodegradation [3, 4].

An example of a biodegradable polymer which undergoes microbial degradation, both in contact with living organisms, and in terms of the natural environment is poly(ε-caprolactone), which can degrade in several biotic environments, including sea, river and lake water, sewage sludge, farm soil and compost [5-12].
According to the literature degradation of poly(ε-caprolactone) in a living environment can result

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of simple chemical hydrolysis of ester bonds or from enzymatic attack or both [13].
Chemical hydrolysis can be resulted in decreasing of molecular weight. Enzymatic degradation takes place only on the polymer surface, and therefore is associated usually with erosion process and may be quantitatively characterized by weight loss and fragmentation of the sample. At the result the polymer is disintegrated in the natural environment. Obviously, disintegradability does not indicate on total sample degradation. The small particles of the sample are constantly degraded and bioassimilated by microorganisms present in the environment, until the samples would be completely converted to carbon dioxide and water.
The aim of this work was an estimation of susceptibility of poly(ε-caprolactone) (PCL) to environmental degradation in different natural environments. The results of PCL degradation in compost, pond, open and harbour area of the Baltic Sea are compared.

2 Experimental

2.1 Material

The commercial poly(ε-caprolactone) film (PCL, M_w= 80000) with the trade name "CAPA 680" used in this work was kindly supplied by Solvay (England).

2.2 Environments

The incubation of PCL samples took place in the several environments under natural weather depending conditions, such as: the compost, pond, open and harbour area of the Baltic Sea. For comparison degradation of PCL samples was also performed under the laboratory conditions in a liquid medium containing sea water with the sodium azide (NaN_3) and in a liquid medium containing pond water with NaN_3.

2.2.1 The compost pile

The compost pile was prepared under natural conditions of municipal waste treatment plant in Gdynia. It consisted of the dehydrated sewage sludge, burnt lime and straw. Burnt lime (0.45kgCaO/1kg dry mass of compost) was added to ravage phatogenic bacterium and eggs parasites, to deacidificate sewage sludge and to convert sludge to compost. The straw was added to maintain the higher temperature of the compost pile and to loosen the structure of the compost pile. The compost pile prepared under natural conditions was not adequately aerated, so it was expected that a combination of conditions from aerobic at the upper part of pile, microaerophilic in the middle part and facultative anaerobic at the bottom of the pile could occur for microorganisms growth [2].
The Figure 1 represents cross-section of compost pile in natural environment.

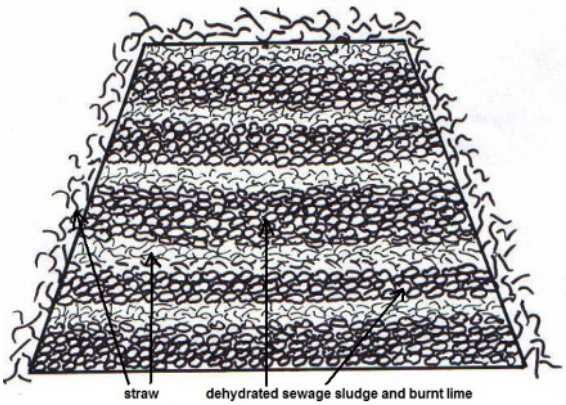

Figure 1. The cross-section of compost pile prepared in natural environment

The PCL samples were put into the special perforated basket and buried of 1 m in depth of the compost pile. The perforated structure of basket allowed for free access of macro, micro-organisms and enzymes existing in this environment to degraded material.

The characteristic parameters of the compost such as: temperature, pH, moisture content, activity of dehydrogenases were measured during environmental degradation process of PCL samples and are shown in Table 1 [9].

Table 1. Characteristic parameters of compost

Months	Parameters			
	temperature [°C]	pH	moisture content [%]	Activity of dehydrogenases [mol mg^{-1} d.m.]
June	17.6	7.8	42.4	0.0197
July	18.2	5.8	45.8	0.0568
August	19.2	6.3	43.5	0.0485

2.2.2 The Baltic Sea water

The incubation of PCL samples took place in two places of the Baltic Sea under natural conditions:
- in the open area of the Baltic Sea in Łeba, on the west side of the western breakwater, in the waters of the East current which allow for constant flow,
- in the harbour area of the Baltic Sea in Gdynia Harbour on the Norwegian Pier near the ship of the Polish Ship Salvage Company.

The PCL samples were located in a special basket made of perforated galvanized steel, which was suspended from a rope at 2 m depth under the surface of the sea. The perforated baskets structure allowed for free movement of seawater and the access of micro-organisms and enzymes dissolved in the water to degraded material.
The places of environmental degradation of PCL in the open and harbour area of the Baltic Sea are shown on Figure 2.

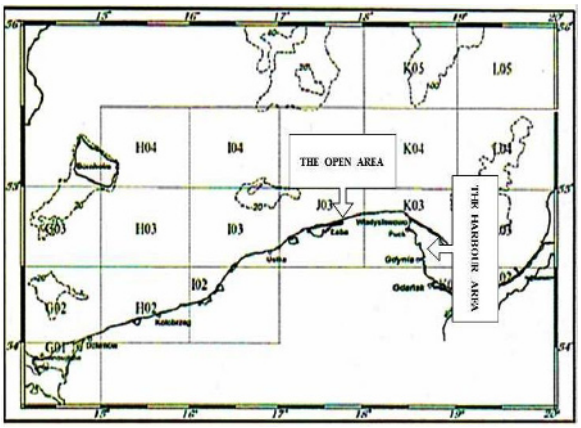

Figure 2. The places of environmental degradation of PCL in the Baltic Sea

The temperature, pH, oxygen and salt content of the Baltic Sea were monitored during environmental degradation process of PCL samples. The characteristic parameters of the sea water in the open and harbour area according to the State Environmental Monitoring, Inspectorate of Environmental Protection are shown in Table 2 and 3 [9, 14].

Table 2. Characteristic parameters of water in open area of the Baltic Sea

Months	Parameters			
	temperature [°C]	pH	oxygen content [cm^3/dm^3]	salt content [ppt]
July	17.8	8.3	6.68	7.50
August	18.6	8.2	6.64	7.53
September	18.2	8.1	6.40	7.46
October	13.7	8.4	6.38	7.75

Table 3. Characteristic parameters of water in harbour area of the Baltic Sea

Months	Parameters			
	temperature [°C]	pH	Oxygen content [cm^3/dm^3]	Salt content [ppt]
June	17.6	8.5	7.55	5.36
July	20.3	8.2	7.57	5.58
August	19.3	8.9	7.42	6.01

2.2.3 The pond

The environmental degradation of PCL samples took place in Rumia's ponds in a special perforated basket at two meters depth under the water surface. The scheme of the pond construction is shown on Figure 3. The Zagórska Struga River is divided into two parts. There are four ponds between that river parts. The basket with polymer samples were located in the one of them.

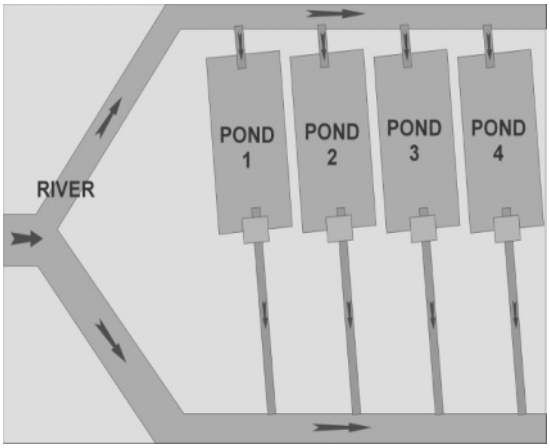

Figure 3. The scheme of the pond construction

The characteristic parameters of the pond such as: temperature, pH were measured during environmental degradation process of PCL samples and are shown in Table 4 [15].

Table 4. Characteristic parameters of water pond under natural conditions

Months	Parameters	
	temperature [°C]	pH
June	17.8	9.0
July	19.3	8.6
August	18.5	8.4
September	12.3	8.5
October	10.0	7.7

2.2.4 The laboratory tests

The degradation of PCL samples was also performed in the laboratory in a liquid medium containing sea water with sodium azide or pond water with sodium azide (NaN_3). The sodium azide (0.195gNaN_3/1000ml) [16] was added to the natural water (derived from a pond or sea) to exclude the activity of micro-organisms and to evaluate the resistance of the polymer to hydrolysis. The PCL samples were located in the glass aquarium equipped with an aeration pump. The characteristic parameters of liquid media under laboratory conditions are shown in Table 5.

Table 5. Characteristic parameters of sea water and water pond under laboratory conditions

Months	sea water with NaN_3		pond water with NaN_3	
	temperature [°C]	pH	temperature [°C]	pH
June	23	8.0	21.7	8.6
July	22	8.1	23.4	6.8
August	23	8.0	21.9	7.7
September	20	8.1	19.5	8.2
October	19	8.0	19.5	7.6

2.3 Measurements

2.3.1 Characterization of the natural environments

The characteristic parameters of the compost, pond and aqueous laboratory environments were measured during degradation process of PCL samples.

2.3.1.1 The humidity of compost

The moisture content of the compost was determined by drying at 105°C until constant weight was obtained.

2.3.1.2 The pH of compost, pond and aqueous laboratory environments

The pH of the compost was determined with a Teleko N 5172 pH-meter.

2.3.1.3 The biochemical activity of compost

To estimate the biochemical activity of microorganisms in sludge, the activity of the dehydrogenases was measured by a spectrophotometric method using triphenyltetrazolium chloride (TTC). The method is based on the dehydrogenation of glucose added to the compost with a subsequent transfer of hydrogen to the colourless biologically active compound of TTC, which undergoes a reduction to triphenyloformazan (TF). The intensity of red colour compound TF was measured using a Specol colorimeter at 490 nm [2, 9].

2.3.2 Investigations of PCL samples

After incubation time the samples were taken out from the environment, washed with distilled water and dried at room temperature until constant weight. The environmental degradability of PCL samples was investigated by changes of weight, surface morphology and crystallinity of polymer after incubation in the each environment.

2.3.2.1 The changes in polymer surface

The morphology of the PCL surfaces was investigated using the optical microscope ALPHAPHOT-2YS2-H Nikon linked to the photo camera Casio QV-2900UX. The view of PCL samples surface before and after degradation was compared. PCL samples were observed with and without polarizer. The pictures were taken before and after incubation in natural and laboratory environment.

2.3.2.2. The changes of weight

The dried samples of PCL were weighed on an analytical electronic balance (Gibertini E 42s, repeatability 0.1 mg). The weight of clean and dried samples of PCL after incubation in the natural and laboratory environment was compared with those before incubation. The percentage weight changes of PCL samples were calculated according to the following equation:

$$x = \frac{m - m_1}{m} \cdot 100 \quad (1)$$

where:
x – changes of weight [%],
m – weight of PCL sample before incubation [g]
m_1 – weight of PCL sample after incubation [g]

2.3.2.3 The changes in crystallinity

The changes of crystallinity PCL samples were also performed based on the differential scanning calorimetry using analyser Setaram Labsys TG-DTA/DSC. The heating scans at the rate of 10°C /min in the temperature range 20–200°C in nitrogen atmosphere, in nitrogen flow 20 cm^3/min were recorded. Based on determined melting enthalpy of PCL samples the percent of crystallinity was calculated [17]. According to the following equation:

$$x = \frac{\Delta H}{\Delta H_{100\%\ PCL}} \cdot 100 \quad (2)$$

where:
x – crystallinity [%],
ΔH - melting enthalpy of PCL sample [J/g]
$\Delta H_{100\%\ PCL}$ – 139.5 [J/g], melting enthalpy of 100% crystalline PCL [18].

3 Results and discussion

3.1 The characteristic of environments

The characteristic of natural environments is determined by its chemical composition and biological properties. Both physico-chemical and biological properties of the environment influence on its suitability for various purposes. Some of them are particularly useful for assessing the quality of environment and occurring in the degradation processes.

Characteristic parameters of all natural environments were monitored during the incubation of polymer samples (Tables 1-4) and their influence on degradation of PCL is discussed.

The temperature of each natural environment was depended on the weather conditions and had been fluctuating a lot during experiment. Only the temperature of natural environments during summer months was more preferable for enzymatic degradation (20-60°C) [19].
Looking at the parameters presented in the Tables 1-4 we can state, that the average temperature in the compost was about 18°C, in the open area of the Baltic Sea – 17°C, in the harbour area – 19°C and in the pond about 16°C.
Temperature fluctuation occurred in the open water of the Baltic Sea. It was connected with the water exchange in this natural environment. The period of water exchange in the open water of the Baltic Sea

is less than 7 days, while in the closed water takes to 52 days [20].
Temperature fluctuations in the pond were related to the small size the water reservoir, which facilitates the heating and cooling of the water pond.
However the average temperature in all natural environments (compost, sea water, pond) was lower as that preferred for enzymatic degradation (20-60°C) [19].

Analyzing characteristic parameters presented in the Tables 1-4 we can also state that there were significant differences in the pH values of all natural environments. The average pH in the compost was slightly acid (pH 6.6), but in the open area value of pH of the Baltic Sea was 8.1, in the harbour area 8.5 and in the pond 8.4. In all liquid natural environments pH was above the upper limit of pH (5-8) recommended in the biodegradation process [19].
The best value of pH for growth bacteria in freshwater is 6-8 [21]. In order to maintain a proper mechanism of water self-purification and a favorable climate for all inhabitants of the pond - the pH should be between 7.4 and 8.4. Water from the pond with a high alkalinity is able to neutralize acidic rainwater supply and the high acidity may be indicative of conditions in which toxic components are activated [22]. The water in the pond must not contain toxic components, especially since in the pond are bred fishes (trouts).

The water has the capacity to dissolve gases. This solubility decreases with increasing temperature and salinity. Pond water is better than sea water. The amount of oxygen depends on the ability of water to the self-cleaning due to the mineralization of organic substances. Mineralization is done with the help of micro-organisms, especially aerobic bacteria. The average concentration of oxygen in the clear river waters in temperate climates is about 5-7mg/dm^3[21].

The rather low temperatures (below 20°C) and slightly acid pH (~6) of compost under natural weather depending conditions (Table 1) caused that psychrotrophic acidophilic microorganisms (fungi) could play the main role in the degradation process. It is known that the most favorable conditions for fungal growth are at a pH below 6 and a high oxygen supply [21].
The activity of dehydrogenases depends on the degree growth of microorganism populations, which are producing enzymes involved in degradation process. During the degradation time of PCL samples the activity of dehydrogenases had been changing and depending on both biotic and abiotic conditions in this environment. The weather, as well as respiration of microorganisms have an influence on fluctuation of moisture content in the compost. With decreasing of moisture content lower absolute value of the activity of dehydrogenases was observed (Table 1).

The Baltic Sea is both a very interesting and complicated natural environment for degradation process because microorganisms, animals, salt, sunlight, fluctuation of water, rain etc. all play a part in degradation in nature.

The relatively low temperature and alkalinity of sea water (Table 2 and 3) could have an influence on the activity of psychrotrophic bacteria, which are able to adapt to so changing conditions.
At the beginning of the summer period of incubation of PCL samples in sea water in the natural environments (June in the harbour area and July in the open area) we could observe the higher oxygen content, than at the end of incubation time. This result is connected with the production of organic matter by micro-organisms, which consumed oxygen contained in the water to degradation processes [2,14].
Looking at the parameters presented in the Table 2 and 3 we can see significant differences in the salinity of both natural environments.
Salt content of the Baltic Sea water is changed naturally and depends on tributary of rivers or heavy rains [20].

Considering the characteristic abiotic parameters of all natural environments: the compost, sea water and pond presented in Tables 1-4 and the different microbial communities (fungi in compost, bacteria in sea water and algae, heterotrophic and epilithic bacteria in pond), we could expect the different rate of environmental degradation of PCL samples.

Incubation of PCL samples in the laboratory in a liquid medium containing sea water with NaN_3 and pond water with NaN_3 (Table 5) was performed in a stable temperature (about 21°C in medium containing sea water and the same in pond water) and under near neutral environment conditions (pH about 7.8-8.0).

3.2 The evaluation of polymer changes during environmental degradation

Susceptibility of PCL to environmental degradation is evaluated based on weight changes [%] of degraded polymer samples. The results of the weight changes of PCL samples after incubation in all natural environments and in the laboratory in a liquid medium containing sea water with NaN_3 or pond water with NaN_3 are presented in Table 6.

Table 6. Weight loss [%] of PCL samples after degradation in natural and laboratory environments

Enviro - nment	Degradation time [weeks]					
	2	**4**	**5-6**	**10**	**12**	**15**
compost	5.6	86.3	disintegration after 5 weeks			
open area of the Baltic Sea	2.2	4.0	8.4	14.9	29.2	disintegra-tion after 12 weeks
harbour area of the Baltic Sea	3.5	20.7	33.8	disintegration after 6 weeks		
pond	-	2.4	3.1	4.0	-	5.6
sea water with NaN_3	1.2	1.4	1.5	1.5	1.5	1.5
pond water with NaN_3	-	1.6	1.9	2.8	-	2.7

[-] not measured at that time

The obtained results testify that PCL degrades in all investigated natural environments such as compost, the Baltic Sea water and pond. It confirms susceptibility

of PCL to biological degradation. Generally, the results presented in Table 6 reflect well, that the environmental degradability of PCL depends on the kind of natural environment – abiotic and biotic parameters.

Disintegration of PCL samples is observed after 5 weeks incubation in compost, 6 weeks in the harbour area of the Baltic Sea and 12 weeks in open area (Table 6). Disintegration, means fragmentation and loss of visibility of samples in natural environment. However, biological degradation has been still continuing. According to the literature polymer samples have been degraded by macro and microorganisms and/or enzymes living in natural environment until they have been converted to carbon dioxide and water [1, 3].

At the beginning of incubation of PCL samples in all natural environments (2 weeks) the small changes of weight (~2-5%) are observed because of similar low temperature conditions (~17^{o}C). The slightly higher changes of weight after incubation of PCL in compost could be caused by different living microbial communities in this environment.

Considering the parameters of compost pile under natural weather depending conditions (temperature and pH) we could state that the psychrotrophic acidofilic microorganisms (fungi) are responsible for the level of degradability of PCL. In contrary to this, there are conditions in the Baltic Sea water, where the low temperature and the alkaline pH are favourable for the development of aerobic psychrotrophic bacteria.

In the next weeks of incubation in the compost and the Baltic Sea water (4-6 weeks) the weight changes of PCL are more visible.

The activity of dehydrogenases in compost influences the variety of microorganisms which are producing enzymes involved in biodegradation process. The parameters presented in Tables 1 show that after 4 weeks of incubation of PCL (July-August) the moisture content and activity of dehydrogenases are higher than in the beginning of incubation. Finally after 5 weeks of environmental degradation PCL samples in compost disintegration is observed.

The higher weight losses of PCL in the harbour than in open area of the Baltic Sea could be caused by different temperature conditions (Table 2 and 3). The temperature of the Baltic Sea water in harbour area was more preferable for enzymatic degradation (20-60^{o}C) [19]. It also suggest, that in the harbour water are probably more favourable conditions to degradation of PCL samples, than those in the open area water. As a result of the higher temperature more visible weight changes and quicker disintegration of PCL samples in the harbour area are observed.

PCL samples have required more time to be destroyed in the pond. After 15 weeks of incubation in natural pond, the weight loss of PCL was only 5.6%. This is most likely related to the high variety of microbial life in the pond (bacteria, protozoa, actinomyces, fungi, algae and fishes), where (at the first) the micro and macroorganisms prefer to consume natural organic compounds present in the environment.

During incubation of PCL in the laboratory medium containing sea water with NaN_3 or in pond water with NaN_3 the weight changes are insignificant even though the temperature was higher, than in natural environment. This was due to an absence of microorganisms in laboratory tests.

The very small changes of weight might be explained by very slow nonenzymatic hydrolytic ester cleavage, what is complied with literature reports that the hydrolytic degradation of PCL is slow because of its hydrophobic nature [23].

One reason of slightly higher weight losses of PCL after incubation in pond water with NaN_3 is the lack of mineral salts which facilitates the diffusion of water within the polymer [24]. Salt contents in laboratory sea water probably have an influence on slow chemical hydrolysis of PCL during incubation in this environment.

The environmental degradation of PCL samples is also evaluated on the basis of changes of surface morphology. After incubation in natural environments the PCL samples were not homogeusly destroyed over the whole polymer surface and there were different images depending on the place the picture was taken.

Photomicrographs of the surface of PCL samples after incubation in all natural environments are presented on Figure 4.

The surface of PCL before incubation when observed under optical microscope is grained and rough (Figure 4a). The microscopic observations after incubation in all natural environments have shown vulnerability of PCL samples to the microbiological attack and deterioration of the surface is observed. The changes of PCL surface during the environmental degradation lead to the erosion (damage) in the form of the observed cracks and holes (Figure 4 b, c, g, e).

Similarly to the changes of weight of the PCL the microscopic observations of surface show that, the rate of changes is faster in compost than in natural aqueous environments (sea and pond water).

The stronger effect of environmental degradation of PCL in compost, than in sea water testify that the psychrotrophic acidophilic microorganisms (fungi) could play the main role in the environmental degradation process.

Noticed faster environmental degradation of PCL in the harbour area of the Baltic Sea is probably because of more favourable temperature conditions for the biodegradation process and lower salinity, which caused the growth of different microorganisms able to degrade PCL samples.

The process of biodegradation in freshwater is carried out with the participation of microorganisms, including bacteria, protozoa, actinomyces and algae [25].

Abiotic parameters of the pond as well as various microbial life in the pond contribute to the slow degradation of PCL (Figure 4 h, i).

The results of changes in crystallinity of PCL samples after incubation in all natural environments are shown on Figure 5.

The changes of PCL crystallinity during incubation in natural environments lead to conclusion that the environmental degradation of PCL occurs in two stages. The first stage consists in the degradation of amorphous phase and as a result an increase

in crystallinity of polymer occurs. The second stage starts when most of the amorphous regions are degraded and subsequently the crystalline phase is degraded. The DSC analysis of PCL samples after degradation in all natural environments revealed the differences in their crystallinity (Figure 5). Only during incubation of PCL in the compost the evident of two-step process of degradation is observed. The higher

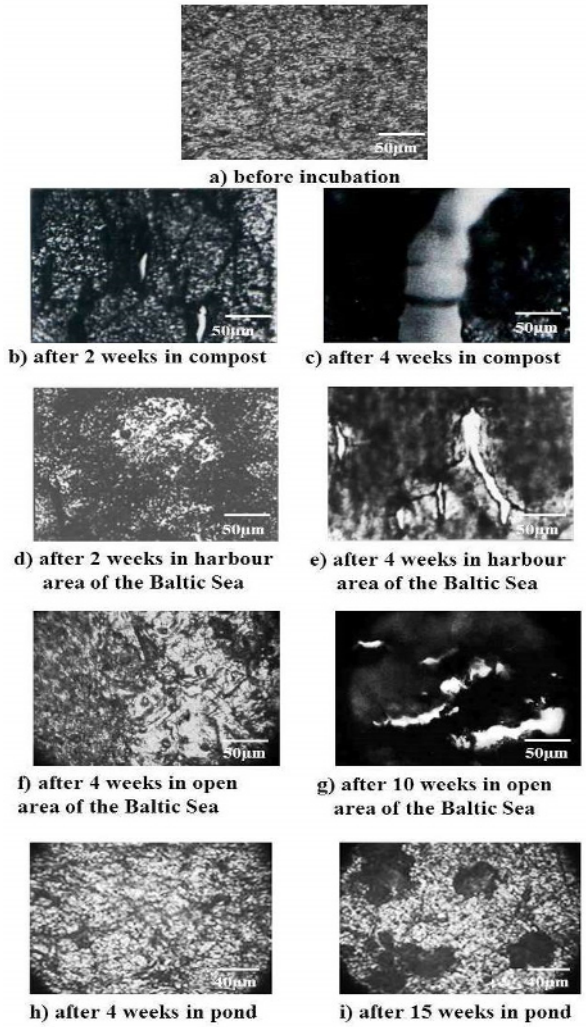

Figure 4. Photomicrographs of the surface of PCL before and after environmental degradation

crystallinity of PCL after 2 weeks of incubation suggests that at first the amorphous phase is degraded, which is accompanied by an increase of crystallinity and next the crystalline phase is degraded (4 weeks).

4 Conclusions

The environmental degradation studies confirm the vulnerability of poly(ε-caprolactone) to the attack of living organisms. The obtained results reveal that the rate of environmental degradation of PCL is dependent on the incubation place, environmental conditions and decreased in order: compost>harbour area of the Baltic Sea>open area of the Baltic Sea>pond.

The characteristic abiotic parameters (temperature, pH, salinity, humidity and oxygenation) of all natural environments and the different microbial communities (psychrotrophic acidofilic microorganisms in compost, psychrotrophic bacteria in sea water and algae, heterotrophic and epilithic bacteria in pond) cause the different rate of environmental degradation of PCL samples.

Disintegration of PCL in the compost is observed faster (after 5 weeks) than in the aqueous environments, because of more favourable biotic and abiotic conditions.

The significant weight loss and erosion of the PCL surface after environmental degradation are the result of enzymatic hydrolysis of ester bonds, which play the key role in the process under natural conditions.

The microscopic changes of PCL surface and crystallinity after incubation in natural environments suggest that the enzymatic degradation of PCL is a two-step process. The first the amorphous phase is degraded, which is accompanied by an increase of crystallinity and next the crystalline phase is degraded.

Insignificant weight losses of the PCL samples incubated in laboratory liquid media may be explained by slow chemical hydrolysis of ester bonds.

The results of research indicate that the degradation of PCL in natural environments such as compost, sea water and pond is the result primarily of enzymatic hydrolysis, which plays a predominant role in the degradation process.

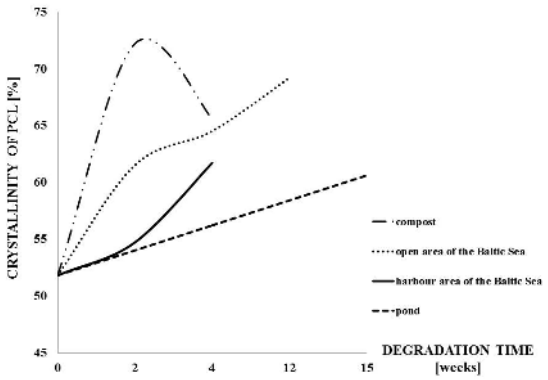

Figure 5. The changes in crystallinity of PCL after environmental degradation

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