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Environmental Degradability of Polyurethanes

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Abstract

The growing interest in environmental issues and increasing demands to develop materials that do not burden the natural environment significantly are currently observed. In this connection many studies on polymer degradation in different environments are carried out. It is important to consider the influence of synergistic action of various factors in order to understand the environmental degradation of synthetic polymers. This requires understanding of interactions between polymer and living organisms.

This paper reviews current authors research on environmental degradation of polyurethanes.

The comparison of environmental degradability of polyurethanes in the Baltic Sea water and compost under natural weather depending conditions is presented. The environmental degradation of poly(ester-urethane) based on poly(ethylene-butylene-adipate) and poly(ester-urethane) based on poly(ϵ -caprolactone) was evaluated.

The characteristic parameters of sea water (temperature, pH, salt, and oxygen contents) and of compost (temperature, pH, moisture content, and activity of dehydrogenases) were monitored and their influence on degradation of polyurethanes was discussed.

The environmental degradability of polyurethanes was investigated by changes of weight, tensile strength, morphology, and crystallinity of polyurethanes after incubation in environment. The investigated polyurethanes were degradable in both natural environments and their environmental degradability depends on the chemical structure and the kind and conditions of environment.

Keywords: Poly(ester-urethane), environmental degradation, sea water, compost

1. Introduction

Polyurethanes are an important and versatile class of synthetic polymers that can be synthesized on a large scale and can be processed in a variety of different ways. For these reasons, polyurethanes are widely used in many aspects of modern life. They have found a widespread use in the industrial fields, for example as furniture coatings, adhesives, construction materials, flame retardants, fibers, paddings, paints, elastomeric parts, and synthetic skins [1-5]. Moreover, over the past 40 years polyurethanes have also been used in various biomedical applications such as vascular prostheses, artificial skin, pericardial patches, soft-tissue adhesive, drug delivery devices, and scaffolds for tissue engineering [6-15].

Polyurethane is a general term used for a class of polymers that are synthesized from three basic components: a diisocyanate, a polyol, and a chain extender. The terminal hydroxyl group allows for alternating blocks, called "segments", to be inserted into polyurethane chain. Soft segments are derived from polyols such as polyester, while the hard segments are formed from the combination of diisocyanate and a chain extender component. The chain extender is usually a small molecule with either hydroxyl or amine groups.

On the one hand, hard segments contribute to hardness, tensile strength, impact resistance, stiffness, and modulus. On the other hand, soft segments contribute to water absorption, elongation, elasticity, softness, and degradability. Hence, from the point of view of applications, it is possible to produce various polyurethanes, which properties can be easily modified by varying structures of soft and hard segments [16].

The nature of polyurethanes chemistry is the central point for understanding why some polyurethanes are non-degradable and other undergo fast degradation. Both non-degradable and degradable polyurethanes can be designed through a proper selection of building segments. Non-degradable polyurethanes are characterized by their excellent chemical stability, abrasion resistance, and mechanical properties. Now despite the xenobiotic origins of polyurethanes, they have been found to be susceptible to degradation by naturally occurring microorganisms.

Degradable polyurethanes are generally achieved by incorporating labile and hydrolysable moieties into polymer chain. It is well known that the biodegradation of polyurethanes depends on their structure, which is conditioned by several factors such as the nature of the used polyol. It has been reported that poly(ester-urethanes) are prone to microbial degradation due to the presence of ester bonds that are known to be enzymatic hydrolysable.

Incorporation of biodegradable fillers or biodegradable aliphatic isocyanates can also enhance biodegradability of polyurethanes and then reduce negative influence on the environment. For example, using a lignin-based polyols in the polyurethanes was observed higher fungal degradation level [17].

Considering the variety of possible applications very often the degradability of polyurethanes has become an important or even a deciding factor. For example, polyurethanes used for

insulation of under-water cables should have high resistance to environmental degradation. In contrast to this, biodegradable polyurethane wastes could be place for utilisation or accumulation in natural environment.

Degradation of polymers is determined by different factors; apart from polymer type the nature of the environment is also important.

The initial breakdown of a polymer, which is the first step of the biological degradation process, can result from physical and biological forces. Physical forces such as heating/cooling, freezing/thawing, or wetting/drying can cause mechanical damage such as cracking of polymeric materials. The growth of many microorganisms can also cause small-scale swelling and bursting of polymeric materials. Most polymers are too large to pass through cellular membranes, so they must be depolymerized to smaller monomers 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. Two categories of enzymes are involved in the biological degradation of polymers: extracellular and intracellular depolymerases. During degradation, exoenzymes from microorganisms break down complex polymers, yielding smaller molecules of short chains that are small enough to pass semi-permeable outer bacterial membranes and then to be utilized as carbon energy sources. Under oxygen conditions, aerobic microorganisms are mostly responsible for the 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 [18].

Figure 1 represents the general mechanism of polymer biological degradation under aerobic conditions in a natural environment such as sea water and compost, which are studied by authors.

According to the literature microorganisms such as fungi and bacteria are involved in the degradation process of polyurethanes [18].

Generally, three types of polyurethane degradations have been identified: fungal degradation, bacterial degradation, and degradation by polyurethanase enzymes. However, polyurethanes are especially susceptible to fungal attack. Soil fungal communities are involved in polyurethanes degradation. For example, four species of fungi, namely, *Curvularia senegalensis*, *Fusarium solani*, *Aureobasidium pullulans* and *Cladosporium*, were obtained from soil and found to degrade ester-based polyurethanes [2, 19]. Bacteria known to degrade poly(ester-urethanes) also produce polyurethanes degrading enzymes, such as polyurethane-esterases. Two kinds of polyurethane-esterase enzymes, such as an intracellular polyurethane-esterase and an extracellular polyurethane-esterase, play predominant and various roles in polyurethane biodegradation process. The intracellular enzyme provides access to the hydrophobic polyurethane surface. Then the extracellular enzyme sticks on the surface of the polyurethane. During these enzymatic actions, the ability of bacteria to adhere to the polyurethanes surface and to hydrolyse polyurethane substrates to metabolites is observed [18].

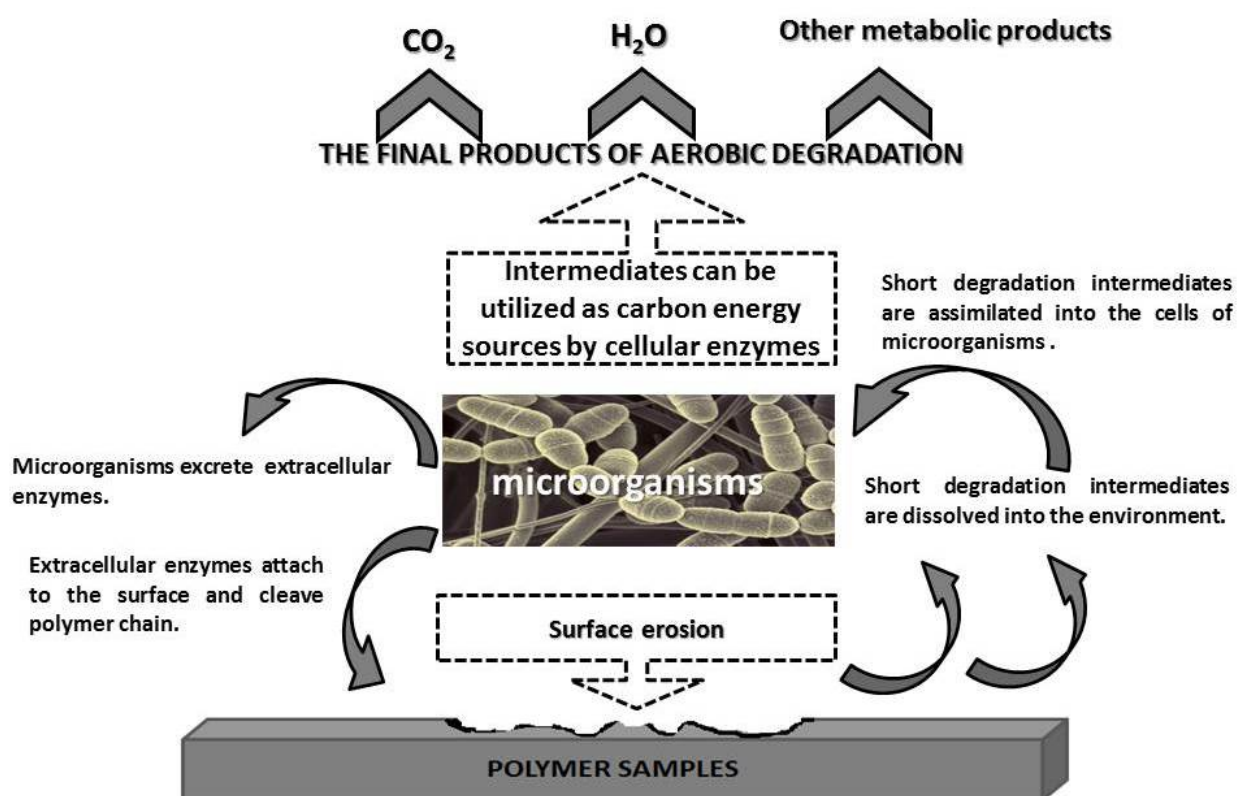


Figure 1. General mechanism of polymer biodegradation under aerobic conditions.

According to the literature, the degradation of polyurethanes is mostly studied in laboratories, in many cases under stable and favourable temperature conditions, providing additional nutrients to microorganisms and using highly concentrated enzymes to promote degradation [2, 4, 6, 8, 17, 20-24].

In the case of degradation in natural environment, very often the synergistic action of various factors leads to polymers degradation. Each natural environment contains different macroorganisms, microorganisms, and enzymes (in terms of species diversity and population). Different physical and chemical parameters, which have influence on rates of microbial activity, affect the rate of the degradation process. Thus, it is very interesting to estimate degradability of polyurethanes under natural weather - depending conditions.

The sea is a very complicated natural environment for degradation because microorganisms, animals, salt, sunlight, fluctuation of water, rain, etc., all play a part in degradation in nature. But it is known that a wide population of living organisms can also exist in the compost. Therefore, sea water and compost under natural weather depending conditions could be used for accumulation and utilization of polyurethane wastes.

The aim of this paper is to summarize and compare the results of environmental degradation of poly(ester-urethanes) in the Baltic Sea water [25] and in compost under natural weather depending conditions [26].

2. Experimental

2.1. Materials

Two kinds of poly(ester-urethanes) were used in this work: poly(ester-urethane)A and poly(ester-urethane)B designated as PU-A and PU-B respectively. The polyurethanes were obtained by a two-step condensation reaction [27, 28].

In the first step, the prepolymers were prepared from 4,4' diphenylmethane diisocyanate /MDI/ and different polydiols. The poly(ethylene-buthylene-adipate) /PEBA/, MW=2000 was used for poly(ester-urethane)A. Poly(caprolactone)diol /PCLD/, MW=2000 was used for poly(ester-urethane)B. The molar ratio of NCO:OH was 4:1 in all cases in the first step reaction. The synthesis was carried out at 80°C. Both prepolymers were further extended by 1,4-butanediol /BD/. A chain extender was added to the prepolymer in an appropriate quantity to maintain a steady NCO:OH ratio of 1.1:1. The content of hard segments (the reaction product of MDI and low molecular weight chain extender) in obtained PU-A and PU-B was 38% [25, 26].

After synthesis, the polymers obtained in a form of a sheet (thickness of 2 mm), were cut into dumbbell-shaped samples and were used for the incubation in the environments.

Before incubation in the environments, the swelling test of polyurethane samples [25] was carried out in acetone and tetrahydrofuran (THF) to estimate the partial solubility and swelling degree, which can inform us about the extent of crosslinking.

Looking at the results of swelling degree and mass loss presented in Table 1, we can notice that PU-A is soluble in THF, PU-B is partially soluble. Thus, both the studied poly(ester-urethanes) differ not only in their chemical structure but in their network as well. PU-B can be partially crosslinked by allophanate bonds while PU-A is uncrosslinked.

Polymer	Equilibrium swelling degree (q)*		Mass loss [%]	
	THF	Acetone	THF	Acetone
PU-A	2.2	Soluble	40	Soluble
PU-B	2.0	6.1	8.0	80

(*) Was calculated from the mass-ratio before and after swelling.

Table 1. Results of swelling test for the blind samples of polyurethanes in acetone and tetrahydrofuran.

2.2. Degradation environments

The incubation of poly(ester-urethanes) took place in two natural environments:

- the Baltic Sea water in Gdynia Harbour
- compost pile under natural weather depending conditions.

The environmental degradation of PU-A and PU-B was carried out for up to 24 months.

During the environmental degradation in the Baltic Sea water, the samples were located in a special basket at 2 m depth under the surface of the sea, near the ship of the Polish Ship Salvage Company. The place of environmental degradation of polyurethane samples in the harbour area of the Baltic Sea is shown on Figure 2.

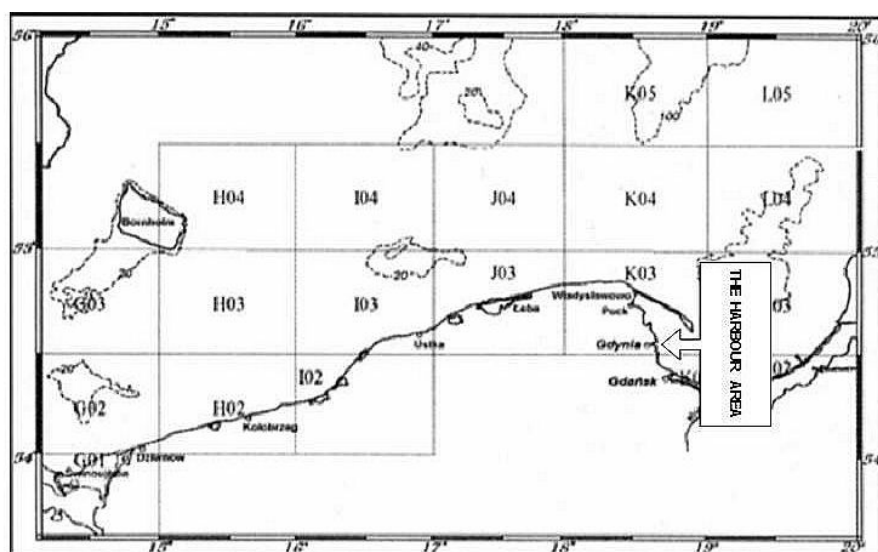


Figure 2. Place of environmental degradation of polyurethane samples in the Baltic Sea.

Degradation of polyurethane samples was also performed in the laboratory in a liquid medium containing sea water with NaN_3 ($0.195 \text{ g NaN}_3/1000\text{cm}^3$). The polyurethane samples were located in the glass aquarium, with dimensions of $40 \times 40 \times 20 \text{ cm}$, equipped with an aeration pump. The sodium azide was added to the sea water to exclude the activity of microorganisms and to evaluate the resistance of the polymers to hydrolysis.

The characteristic parameters of sea water according to the Gdynia Water Management and Meteorology Institute and of liquid medium containing sea water with NaN_3 are shown in Table 2.

Months	PARAMETERS					
	Baltic Sea water			sea water with NaN_3		
	Temperature [°C]	pH	Oxygen contents [cm^3/dm^3]	Salt contents [ppt]	Temperature [°C]	pH
January	2.5	8.2	9.7	6.9	18.0	8.1
February	1.6	8.2	10.3	6.4	18.5	8.0
March	3.5	8.2	10.3	6.5	19.0	8.0
April	5.1	8.4	10.0	6.8	20.0	8.0
May	13.1	8.5	8.5	6.2	21.5	8.0
June	16.5	8.3	8.0	6.3	23.0	8.0

Months	PARAMETERS					
	Baltic Sea water				sea water with NaN_3	
	Temperature [°C]	pH	Oxygen contents [cm^3/dm^3]	Salt contents [ppt]	Temperature [°C]	pH
July	19.4	8.1	7.6	6.1	22.0	8.1
August	20.1	8.2	6.5	6.1	23.0	8.0
September	16.2	8.2	6.7	6.5	20.0	8.1
October	13.1	8.1	6.7	7.1	19.0	8.1
November	6.7	8.2	7.8	6.7	18.0	8.1
December	3.4	8.2	8.0	6.7	18.0	8.0

Table 2. The characteristic parameters of the Baltic Sea water and sea water with NaN_3 .

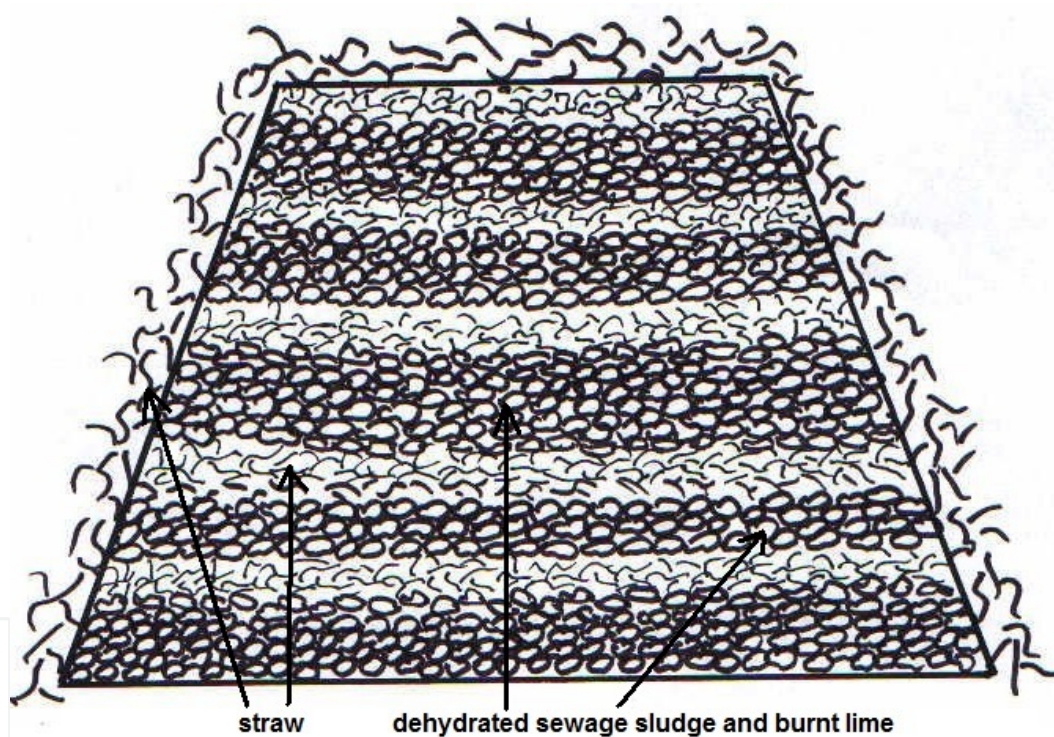


Figure 3. The cross-section of the compost pile prepared in natural environment [26].

The compost used in this work was formed with the dehydrated sewage sludge taken from a municipal waste treatment plant in Gdynia. The compost pile was prepared under natural conditions of sewage farm. It consisted of the sewage sludge, burnt lime, and straw. Burnt lime ($0.45 \text{ kgCaO}/1\text{kg}$ dry mass of compost) was added to ravage pathogenic 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 is 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 microorganism growth [26]. Figure 3 represents cross-section of the compost pile in natural environment.

The characteristic parameters of the compost, such as, temperature, pH, moisture content, and activity of dehydrogenases, were measured during the degradation process and are shown in Table 3.

Months	PARAMETERS			
	Temperature [°C]	pH	Moisture content [%]	Activity of dehydrogenases [mol mg ⁻¹ d.m.]
January	6.0	5.3	49	0.0281
February	4.0	5.6	50	0.0286
May	15.0	5.7	55	0.0297
July	19.0	5.5	53	0.0328
August	22.0	5.4	56	0.0431
November	8.0	5.8	60	0.0318
December	7.0	5.9	55	0.0192

Table 3. The characteristic parameters of compost.

2.3. Measurements

2.3.1. Characterization of the compost pile under natural conditions

The characteristic parameters of the compost such as temperature, pH, moisture content, and activity of dehydrogenases were measured during degradation process.

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 the compost

The pH of the compost was determined with a Teleko N 5172 pH-meter [26].

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 triphenylformazan (TF). The intensity of red colour compound TF was measured using a Specol colorimeter at 490 nm [26].

2.3.2. Investigations of polyurethanes 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 polyurethanes was investigated by changes of weight, tensile strength, morphology, and crystallinity of polyurethane samples after incubation in the environment.

2.3.2.1. The changes in the polymer surface

The changes of polyurethanes surface were evaluated at macro- and micro scale. The views of polyurethane samples surface before and after degradation were compared. The pictures were taken before and after incubation in the environment. Microscopic observations of samples surface were done at magnification of 1:300 using the optical microscope ALPHAPHOT-2YS2-H Nikon linked to the photo camera Casio QV-2900UX. The samples were observed with and without polarizer.

2.3.2.2. The changes of weight

Weight changes were determined using an electronic balance Gibertini E 42s. The weight of clean and dried samples of polyurethanes after incubation in the compost was compared with those before incubation. The percentage weight changes [%] were calculated from the weight data.

2.3.2.3. The changes of tensile strength

Tensile strength [MPa] was measured at room temperature using a Tensile Testing Machine ZMGi-250 according to PN-EN ISO Standard [29].

2.3.2.4. The changes of thermal properties

Thermal analysis was carried out using Perkin-Elmer Pyris 1 Differential Scanning Calorimeter equipped with Intracooler 2P. The heating scans at the rate of 5 K/min in the temperature range -65-230°C in nitrogen atmosphere were recorded [26].

3. Results and discussion

3.1. Characteristics of the degradation environments of polyurethanes samples

The characteristic parameters of the Baltic Sea water and compost pile under natural conditions were monitored during the environmental degradation process of polyurethanes and their

influence on degradation of polyurethanes was discussed. As both biotic and abiotic parameters of sea water (temperature, pH, salinity, and oxygen content) and compost (temperature, pH, moisture content, and activity of dehydrogenases) have a significant influence on the development of living microorganisms in natural environment.

Looking at the parameters presented in Tables 2 and 3, we can state, that the average temperature in the Baltic Sea was about 10°C and about 12°C in the compost pile. The temperature of both environments, depending on the weather conditions (season), had been fluctuating a lot during the experiment (from 1 to 20°C in sea water and 1°C-22°C in compost). Only the average temperature of sea water and compost during summer months (July, August) was on the similar level to the preferred for enzymatic degradation (20°C-60°C) [30].

There were significant differences in the pH values of both natural environments. The average pH in the Baltic Sea was 8.2 and 5.5 in compost pile.

The very low temperature and the alkaline pH (~8) of the Baltic Sea caused that the psychrotrophic bacteria could play the main role in the degradation in this environment [25].

During the winter months, we could observe the very low temperature and the highest oxygen content (February 10, 3 cm³/dm³). These conditions could have an influence on the activity of oxidizing enzymes, which are responsible for oxidation. It could be expected that these conditions had an influence on the development of aerobic epilithic bacteria. The metabolism of these microorganisms probably caused the decrease of oxygen content in the summer months (August 6.5 cm³/dm³) and changed the concentration of carbon dioxide in sea water. However, it was not able to change significantly the pH of sea water.

It is known that the activity of dehydrogenases depends on the degree growth of microorganism populations, which are producing enzymes involved in degradation process. During the degradation time, 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, had an influence on fluctuation of moisture content in the compost. With decreasing moisture content, lower absolute value of the activity of dehydrogenases was observed.

The rather low temperatures (below 20°C) and slightly acid pH (~6) of compost under natural weather - depending conditions caused that psychrotrophic acidophilic microorganisms (fungi) could play the main role in the degradation process [26].

Considering the characteristic abiotic parameters of sea water and compost presented in Tables 1 and 2 and the different microbial communities (fungi in compost and bacteria in sea water), we could expect the different rate of degradation of polyurethanes in these two natural environments.

Incubation of polyurethane samples in the laboratory in a liquid medium containing sea water with NaN₃ (Table 2) was performed in a stable temperature (about 20°C) and under alkaline conditions (pH about 8).

3.2. Evaluation of the changes of polyurethane samples during environmental degradation

The environmental degradation of polyurethanes in sea water and compost was evaluated visually at first. Figure 4 represents the surface view at macro scale of investigated poly(ester-urethanes) before and after degradation in the Baltic Sea water and compost under natural weather depending conditions.

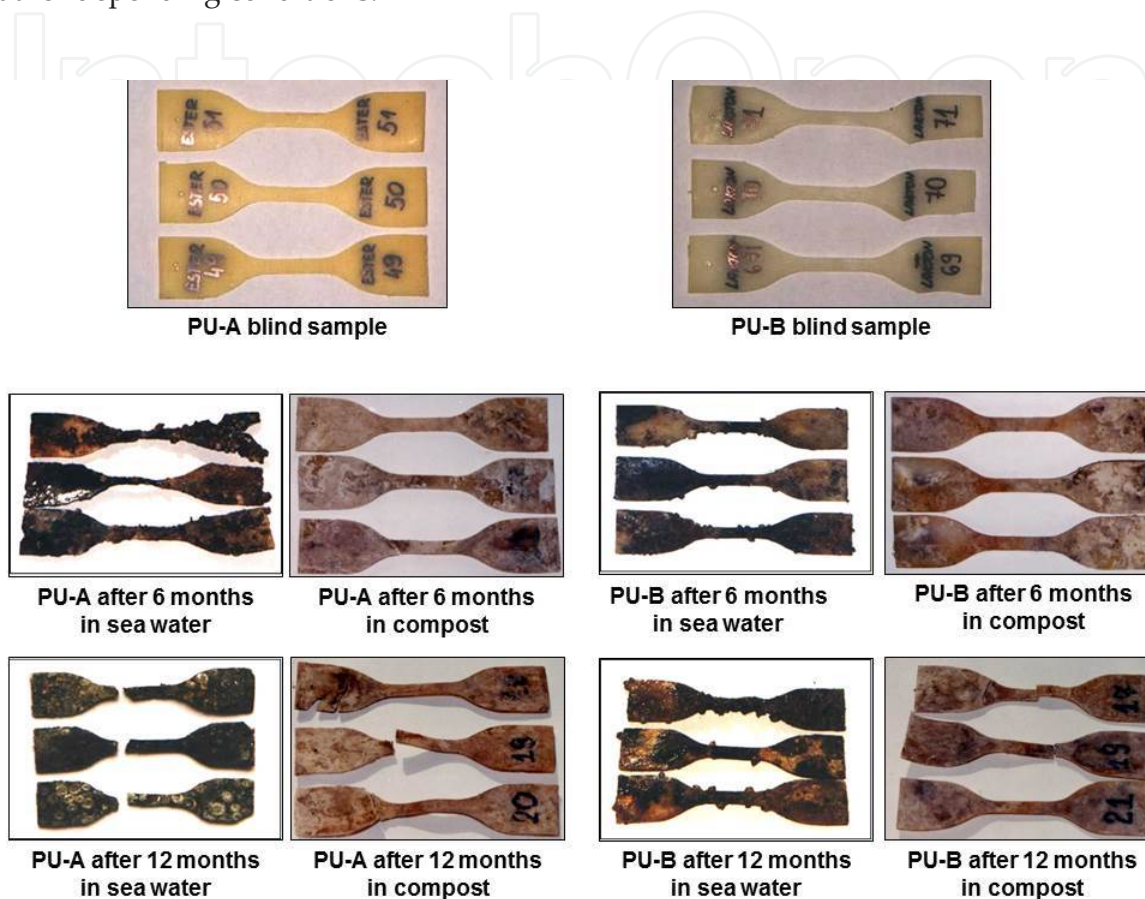


Figure 4. Macroscopic images of poly(ester-urethanes) after environmental degradation.

The blind samples of PU-A and PU-B are beige or white and opaque. The both poly(ester-urethane) samples incubated in natural environments are characterized by the flaws at the surface that gradually grew into microcracks, eventually breaking the samples. At the end of the experiment in natural environments, the surface of poly(ester-urethanes) samples is rough and cracked with visible black areas after incubation in sea water. While after incubation in sea water with NaN_3 the surface is only matt.

The environmental degradation of poly(ester-urethane) samples in the Baltic Sea water and the compost under natural weather-depending conditions was also evaluated on the basis of changes of surface morphology. After incubation in both natural environments, the poly(ester-urethane) samples were not homogeneously destroyed over the whole polymer surface and there were different images depending on the place. The photomicrographs repeated images observed under the reflected microscope equipped with polarizer were done.

Microscopic observations after incubation in the natural environments have shown vulnerability of PU-A and PU-B to the microbiological attack. The changes of surfaces of both poly(ester-urethanes) are comparable. After incubation of poly(ester-urethanes) in natural environments the deterioration of the surfaces has been observed. The photomicrographs of PU-B are presented in Figure 5.

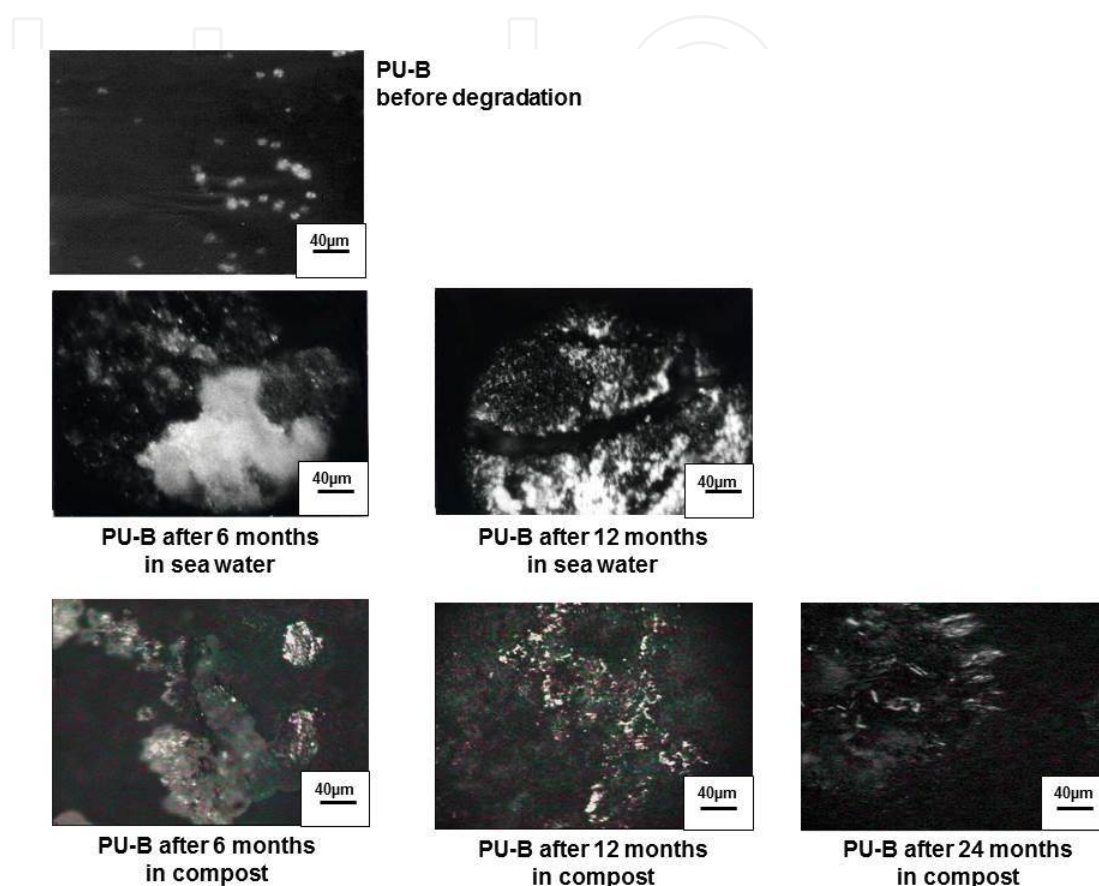


Figure 5. Microscopic images of PU-B observed under optical microscope with polarizer before and after environmental degradation.

The changes in birefringence of PU-B observed under a polarized optical microscope are noticeable (Figure 5). The blind sample of PU-B is slightly crystalline (the bright elements on the surface before degradation). It is known that the degradation process of polyesters proceeds in two stages [31]. During the first stage of the environmental degradation of PU-B, the gradually increase of bright elements on the surface was observed. This increase of bright elements might be an evidence of increase in crystallinity as a result of the degradation amorphous phase (random hydrolytic scission of ester bonds) [25, 26]. The second stage started after degradation of the major part of the amorphous phase. At the end of incubation in the compost, we could see distinct loss of bright elements due to the degradation of the crystalline phase (Figure 5).

Comparing microscopic observations of PU-B after environmental degradation in the Baltic Sea water and in compost we can state that PU-B based on poly(ϵ -caprolactone) is more

vulnerable to degradation in compost than in sea water. Thus, the higher deterioration of the PU-B surface have been observed. It is because of the fragment of poly(ϵ -caprolactone) in the main chain of PU-B, which is susceptible to microbial degradation. Moreover, in this natural environment there were conditions favourable for growth of fungi. It is well known that fungal communities are involved in poly(ester-urethanes) biodegradation [2, 6, 17, 23, 24, 32].

Susceptibility of poly(ester-urethanes) to environmental degradation was evaluated based on weight changes [%] of polymer samples after incubation. The results of the weight changes of the PU-A and PU-B after incubation in natural environments are presented in Figure 6.

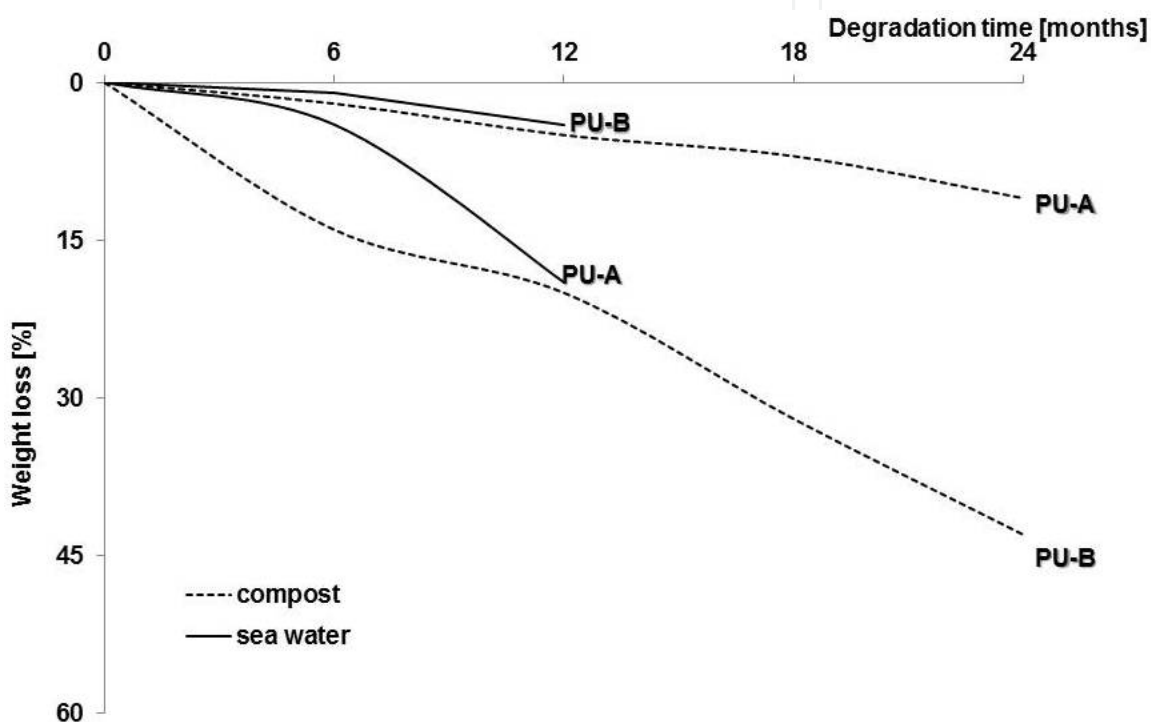


Figure 6. The weight losses [%] of PU-A and PU-B after environmental degradation.

The obtained results indicate that both poly(ester-urethanes) degrade in natural environments such as the Baltic Sea water and compost. It confirms susceptibility of poly(esters-urethane) to biological degradation.

Generally, the results presented in Figure 6 indicate that the degradability of poly(ester-urethanes) depends on their chemical structure and the kind of environment.

In the Baltic Sea water, where the low temperature and the alkaline pH were favourable for the development of aerobic bacteria, uncrosslinked PU-A based on poly(ethylene-butylene-adipate) was more prone to degradation than PU-B based on poly(ϵ -caprolactone). At the end of incubation in the Baltic Sea water (12 months) the changes of weight of PU-A were much higher (19%) than of PU-B (4%). It could be explained by the different networks of those polyurethanes. Unexpectedly, the introduction of a fragment of poly(ϵ -caprolactone) to the main chain of PU-B did not lead to the increase of its environmental degradability [25].

In contrary, to this there are results of the degradation of poly(ester-urethanes) in compost under natural weather-depending condition. The strongest effect of environmental degradation in compost was observed for slightly crosslinked PU-B based on poly (ϵ -caprolactone) than not crosslinked PU-A based on poly(ethylene-butylene-adipate). It could be mainly explained by degradation of poly (ϵ -caprolactone) in this biotic environment as a result of enzymatic hydrolysis of ester bonds susceptible to fungal degradation [26]. Considering the parameters of compost pile under natural weather-depending conditions (temperature and pH) it could be stated that the psychrotrophic acidophilic microorganisms (fungi) were responsible for the level of degradability of poly (ester-urethanes).

According to the literature polyester degradation occurs primarily by chain scission in main chain of polymer and can be induced by enzymatic hydrolysis. Enzymes can attack on the surface poly(ϵ -caprolactone) segments of polyurethane, degrading them to smaller molecular units via hydrolytic attack. Then surface erosion takes place with farther hydrolysis process erosion. At the end, hydrolysis rate decreases after the consumption of the amorphous materials by microorganisms [6, 33, 34].

This is why the higher weight losses and deterioration of the surface have been observed during environmental degradation in compost [26].

During incubation in the sea water with NaN_3 in the laboratory, the weight changes of poly(ester-urethane)s are insignificant even though the temperature was higher than in the natural environment. This was due to the absence of microorganisms in sea water with sodium azide [25].

Changes of mechanical properties of both poly(ester-urethanes) were checked by the measurement of the tensile strength before and after environmental degradation. The results are presented in Figure 7.

It is interesting to note that for blind samples, the higher tensile strength is observed for PU-B sample, which is due to its partial crosslinking. The rates of the changes in the mechanical properties (Figure 7) resemble the rate of the mass loss (Figure 6) and the changes of surface poly(ester-urethanes) (Figures 4 and 5). The data in Figure 7 show that the tensile strength of poly(ester-urethanes) had been decreased during the incubation time in sea water and compost [25, 26]. After 6 months of environmental degradation, only the samples of PU-A incubated in sea water were torn up into pieces, whereas the tensile strength of the other samples degraded in both environments could still be estimated. Probably, microorganisms existed in sea water, such as psychrotrophic bacteria, caused the breaking of polymer samples resulting in the fragmentation. After 12 months of environmental degradation all poly(ester-urethanes) lost the tensile strength.

The loss of tensile strength, discoloration, and cracking observed for environmental degraded poly(ester-urethanes) are typical for the effects of degradation of poly(ester-urethanes) as a result of microorganisms activity.

The results of thermal analysis of poly(ester-urethane) samples are shown in Table 4 and Figure 8a and b and they are in the agreement with microscopic observations (Figure 5).

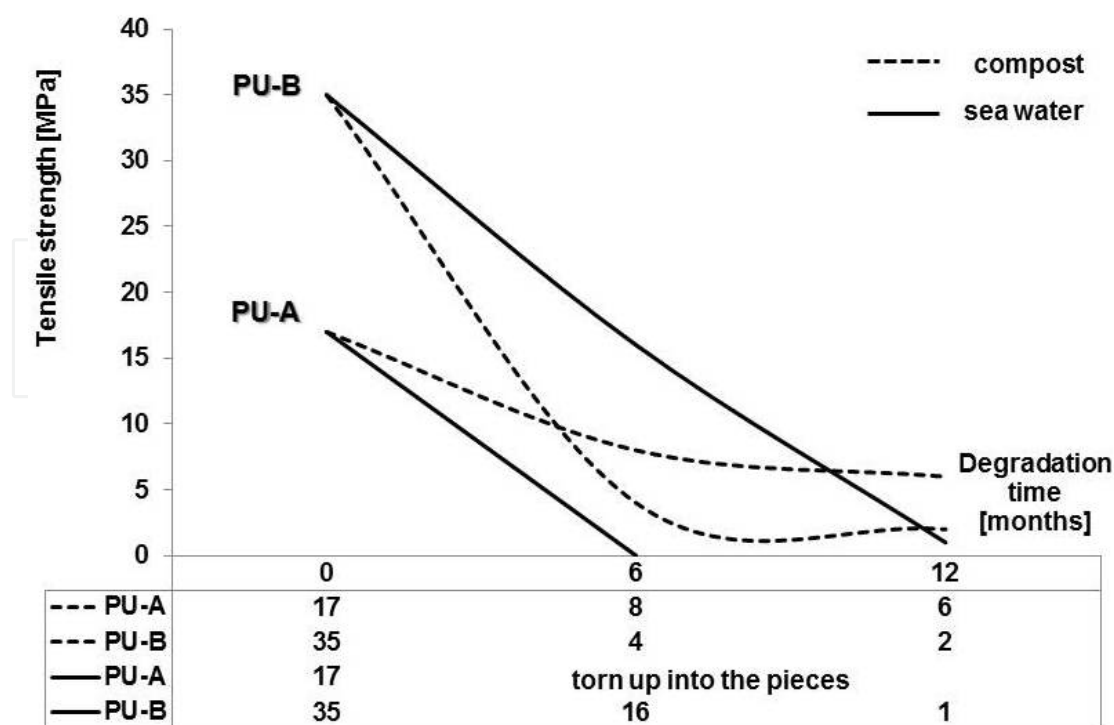


Figure 7. The tensile strength [MPa] of PU-A and PU-B before and after environmental degradation.

Polymer	Incubation time [months]	T _{mSS} [°C]	ΔH _{SS} [J/g]	T _{mHS} [°C]	ΔH _{HS} [J/g]
PU-A	0	-	-	140/184	3/3
	6	48	8	146	39
	12	51	9	136	2.3
	24	55	8	151	22
PU-B	0	77	2.6	-	-
	6	49	5.5	188	3
	12	50	3	143/196	2/1
	24	52	7.6	189	2

Table 4. Melting temperature (T_m) and melting enthalpy (ΔH) of crystallites made of soft (SS) and hard segment (HS) determined from DSC scans for PU-A and -B samples before and after incubation in compost.

The DSC analysis of PU-A and PU-B revealed the differences in their phase composition (Figure 8). Both poly(ester-urethanes) before degradation showed the little presence of crystal phases. The blind sample of PU-A contains mainly crystals made of hard segments, which is indicated by the small melting peaks at high temperatures (140°C and 184°C in Figure 8a). In the case of the blind sample of PU-B, only small melting peak at low temperatures (77°C in Figure 8b) was noticed. It is corresponding to the melting of soft segments crystals.

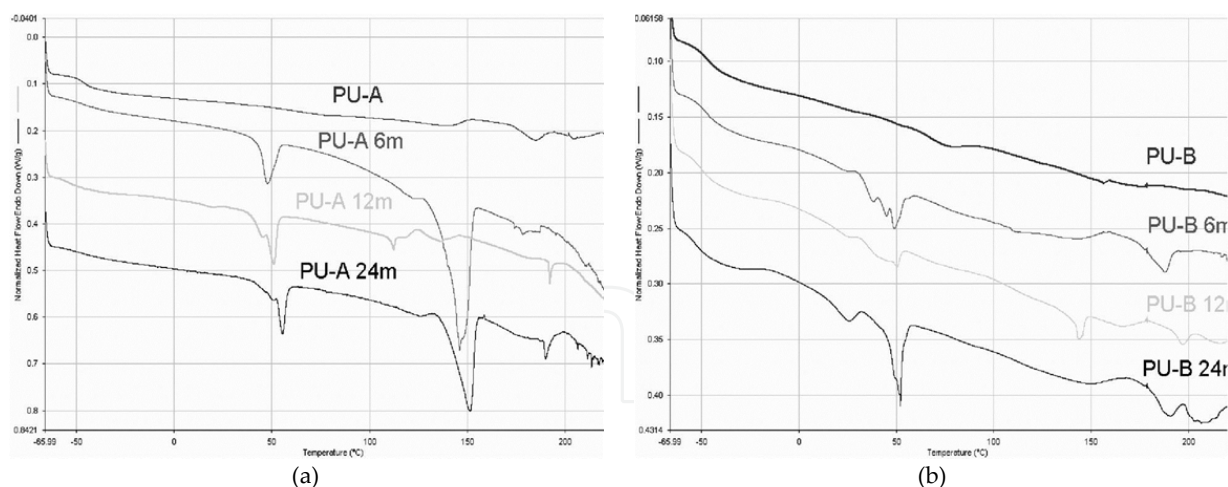


Figure 8. The DSC curves for poly(ester-urethanes): **a)** PU-A and **b)** PU -B before and after incubation in the compost for 6, 12, and 24 months [26]

Due to incubation in the compost, the evident increase in crystallinity in both poly(ester-urethanes) was observed. However, in the case of PU-A, crystal phases made of both hard and soft segments appeared, but in the case of PU-B, mainly crystal phase made of soft segments (compare Figure 8a and b and Table 4) appeared. The observation that higher crystallinity develops in PU-A may be explained by its uncrosslinked structure. In the case of PU-B, the partial crosslinking constraints at some point of crystallization are especially of hard segments. Differences in crystallinity in both poly (ester-urethanes) seem to correspond with mechanical properties. The smaller decrease of mechanical properties of PU-A is due to the reinforcing effect of higher crystallinity [26].

4. Conclusions

Currently, the information concerning microbial degradation of polyurethanes in the natural environment is still limited. In this study, the ability of the Baltic Sea water and compost to degrade poly(ester-urethanes) were accessed. The achieved results pointed out that the poly(ester-urethane) based on poly(ethylene-butylene-adipate) and poly(ester-urethane) based on poly (ϵ -caprolactone) are susceptible to environmental degradation under natural weather-depending conditions.

Generally the stronger effect of environments degradation—the higher weight losses and deterioration of the surface of poly(ester-urethanes)—has been observed during environmental degradation in compost, than in sea water where the conditions were favourable for the development of aerobic bacteria.

In the Baltic Sea water uncrosslinked poly(ester-urethane) based on poly(ethylene-butylene-adipate) was very prone to degradation. Whereas slightly crosslinked poly(ester-urethane) was moderately resistant to degradation in sea water, even though it has a fragment of poly (ϵ -caprolactone) in the main chain. In contrary to this, there are results of the degradation of

poly(ester-urethanes) in compost. In this environment, slightly crosslinked poly(ester-urethane)B, based on poly(ϵ -caprolactone) was more degradable, than not being crosslinked poly(ester-urethane)A, based on poly(ethylene-butylene adipate). Finally, the higher weight losses and deterioration of surface have been observed. It could be mainly explained by degradation of poly (ϵ -caprolactone) in this biotic environment as a result of enzymatic hydrolysis of ester bonds susceptible to fungal degradation. The psychrotrophic acidophilic microorganisms (fungi) were responsible for the level of degradability of poly(ester-urethanes) in compost.

Due to incubation in the compost, there is the evident increase in crystallinity in both poly(ester-urethanes). Differences in crystallinity are corresponding with mechanical properties as reinforcing effect of crystal phase in poly(ester-urethanes). The smaller decrease in mechanical properties of poly(ester-urethane)A, than poly(ester-urethane)B may be due to its higher crystallinity. The loss of tensile strength, discoloration, and cracking observed for environmental degraded poly(ester-urethanes) are typical for the effects of degradation of poly(ester-urethanes) as a result of microorganisms activity.

The environmental degradation process of poly(ester-urethanes) indicates that the degradation in natural environment such as the Baltic Sea water and compost is the result primarily of enzymatic hydrolysis of ester bonds, then crystallinity and network structure of poly(ester-urethanes). The rate of environmental degradation process of poly(ester-urethanes) also is depended on the kind and conditions of natural environment.

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References

- [1] Wood G, editor. The ICI polyurethanes book. 2nd ed. New York: Wiley & Sons Inc.; 1990.
- [2] Howard GT. Biodegradation of polyurethane: A review. *International Biodeterioration & Biodegradation*. 2002;49:245-252. DOI: 10.1016/S0964-8305(02)00051-3.
- [3] Zhang Y, Xia Z, Huang H, Chen H. A degradation study of waterborne polyurethane based on TDI. *Polymer Testing*. 2009;28:264-269. DOI: 10.1016/j.polymertesting.2008.12.011.

- [4] Umare SS, Chandure AS. Synthesis, characterization and biodegradation studies of poly(ester urethane)s. *Chemical Engineering Journal*. 2008;142:65-77. DOI: 10.1016/j.cej.2007.11.017.
- [5] Gao X, Guo Y, Tian Y, Li S, Zhou S, Wang Z. Synthesis and characterization of polyurethane/zinc borate nanocomposites. *Colloids Surfaces A-Physicochemical and Engineering Aspects*. 2011;384:2-8. DOI: 10.1016/j.colsurfa.2010.11.037.
- [6] Cometa S, Bartolozzi I, Chellini F, Giglio E, Chiellini E. Hydrolytic and microbial degradation of multi-block polyurethanes based on poly(caprolactone)/poly(ethylene glycol) segments. *Polymer Degradation and Stability*. 2010;95:2013-2021. DOI: 10.1016/j.polymdegradstab.2010.07.007.
- [7] Pretsh T, Jakob I, Muller W. Hydrolytic degradation and functional stability of a segmented shape memory poly(ester urethane). *Polymer Degradation and Stability*. 2009;94:61-73. DOI: 10.1016/j.polymdegradstab.2008.10.012.
- [8] Yeganeh H, Hojati-Talemi P. Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol). *Polymer Degradation and Stability*. 2007;92:480-489. DOI: 10.1016/j.polymdegradstab.2006.10.011.
- [9] Lelah MD, Cooper SL. *Polyurethanes in medicine*. Boca Raton, Florida: CRC Press Inc.; 1986.
- [10] Planck H, Syre I, Dauner M, Egbers G, editors. *Polyurethane in biomedical engineering*. 2nd ed. Amsterdam: Elsevier Science Ltd; 1987.
- [11] Cherng JY, Hou TY, Talsma H, Hennik WE. Polyurethane-based drug delivery system. *International Journal Of Pharmaceutis*. 2013;450:145-162. DOI: 10.1016/j.ijpharm.2013.04.063.
- [12] Ding M, Li J, Tan H, Fu Q. Self-assembly of biodegradable polyurethanes for controlled delivery applications. *Soft Matter*. 2012;8:5414-5428. DOI:10.1039/C2SM07402H.
- [13] Guelcher SA, Srinivasan A, Dumas JE, Didier JE, McBride S, Hollinger JO. Synthesis, mechanical properties, biocompatibility and biodegradation of polyurethane networks from lysine polyisocyanates. *Biomaterials*. 2008;29:1762-1775. DOI: 10.1016/j.biomaterials.2007.12.046.
- [14] He X, Zhai Z, Wang Y, Wu G, Zheng Z, Wang Q, Liu Y. New method for coupling collagen on biodegradable polyurethane for biomedical application. *Journal of Applied Polymer Science*. 2012;126:E353-E360. DOI: 10.1002/app.36742.
- [15] Zdrahala RJ, Zdrahala IJ. Biomedical applications of polyurethanes: A review of past promises, present realities, and a vibrant future. *Journal of Biomaterials Applications*. 1999;14:67-90. DOI: 10.1177/088532829901400104.
- [16] Young RJ, Lovell PA, editors. *Introduction to polymers*. 2nd ed. London: Chapman & Hall; 1994.

- [17] Amaral JS, Sepulveda M, Cateto CA, Fernandes IP, Rodrigues AE, Belgacem MN, Barreiro MF. Fungal degradation of lignin-based rigid polyurethanes foams. *Polymer Degradation and Stability*. 2012;97:2069-2076. DOI: 10.1016/j.polymdegradstab.2012.03.037.
- [18] Shah AA, Hasan F, Hameed A, Ahmed S. Biological degradation of plastics: A comprehensive review. *Biotechnology Advances*. 2002;28:246-265. DOI: 10.1016/j.biotechadv.2007.12.005.
- [19] Eubeler JP, Bernhard M, Knepper TP. Environmental biodegradation of synthetic polymers II. Biodegradation of different polymer group. *Trends in Analytical Chemistry*. 2010;29:84-100. DOI: 10.1016/j.trac.2009.09.005.
- [20] Gorna K, Gogolewski S. In vitro degradation of novel medical biodegradable aliphatic polyurethanes based on caprolactone and Pluronics with various hydrophilicities. *Polymer Degradation and Stability*. 2002;75:113-122. DOI:10.1016/S0141-3910(01)00210-5.
- [21] Khan I, Smith N, Jones E, Finch DS, Cameron RE. Analysis and evaluation of a biomedical polycarbonate urethane tested in an in vitro study and an ovine arthroplasty model. Part I: Materials selection and evaluation. *Biomaterials*. 2005;26:621-631. DOI: 10.1016/j.biomaterials.2004.02.065.
- [22] Urgun-Demirtas M, Singh D, Pagilla K. Laboratory investigation of biodegradability of a polyurethane foam under anaerobic conditions. *Polymer Degradation and Stability*. 2007;92:1599-1610. DOI: 10.1016/j.polymdegradstab.2007.04.013.
- [23] Lu H, Sun P, Zheng Z, Yao X, Wang X, Chang FC. Reduction-sensitive rapid degradable poly (urethane-urea)s based on cystine. *Polymer Degradation and Stability*. 2012;97:661-669. DOI: 10.1016/j.polymdegradstab.2011.12.023.
- [24] Tatai L, Moore TG, Adhikari R, Malherbe F, Jayasekara R, Griffiths I, Gunatillake PA. Thermoplastic biodegradable polyurethanes: The effect of chain extender structure on properties and in vitro degradation. *Biomaterials*. 2007;28:5407-5414. DOI: 10.1016/j.biomaterials.2007.08.035.
- [25] Rutkowska M, Krasowska K, Heimowska A, Steinka I, Janik H. Degradation of polyurethanes in sea water. *Polymer Degradation and Stability*. 2002;76:233-239. DOI: 10.1016/S0141-3910(02)00019-8.
- [26] Krasowska K, Janik H, Gradys A, Rutkowska M. Degradation of polyurethanes in compost under natural conditions. *Journal of Applied Polymer Science*. 2012;125:4252-4260. DOI: 10.1002/app.36597.
- [27] Rutkowska M, Balas A. Influence of NCO:OH relation and chain extender on primary and secondary valence crosslinks in urethane elastomers. *Journal of Applied Polymer Science*. 1980;25:2531-2538. DOI: 10.1002/app.1980.070251108.

- [28] Rutkowska M, Eisenberg A. Ionomeric blends. IV. Miscibility of urethane elastomers with styrene-styrene sulfonic acid copolymer. *Journal of Applied Polymer Science*. 1984;29:755-762. DOI: 10.1002/app.1980.070290304.
- [29] PN-EN ISO 527-1,2,3:1998, *Plastics—Determination of Tensile Properties*.
- [30] Lenz RW. *Biodegradable Polymers*. In: *Advances in Polymer Science*. Berlin: Springer-Velay; 1993. p. 1-40.
- [31] Li S, Vert M. *Biodegradation of Aliphatic Polyesters*. In *Degradable Polymers Principles and Applications*. 2nd ed. UK: Kluwer Academic Publisher; 2002. p. 71-132. DOI: 10.1007/978-94-017-1217-0.
- [32] Barrat SR, Ennos AR, Greenhalgh m, Robson GD, Handley PS. Fungi are predominant micro-organisms responsible for degradation of soil-buried polyester polyurethane over a range of soil water holding capacities. *Journal of Applied Microbiology*. 2003;95:78-85. DOI: 10.1046/j.1365-2672.2003.01961.x.
- [33] Zhou L, Liang D, He X, Li J, Tan H, Fu Q, Gu Q. The degradation and biocompatibility of pH-sensitive biodegradable polyurethanes for intracellular multifunctional antitumor drug delivery. *Biomaterials*. 2012;33:2734-2745. DOI: 10.1016/j.biomaterials.2011.11.009.
- [34] Khan S. *Biodegradation of polyurethane by bacterial consortium*. *Elixir Bio Technology*. 2011;37:3767-3772.