

Degradation of Polyurethanes in Compost under Natural Conditions

Katarzyna Krasowska,¹ Helena Janik,² Arkadiusz Gradys,³ Maria Rutkowska¹

¹Department of Chemistry and Industrial Commodity Science, Gdynia Maritime University, 83 Morska Str. Gdynia 81-225, Poland

²Department of Polymer Technology, Chemical Faculty, Gdansk University of Technology, 11/12 Narutowicza Str. Gdansk 80-952, Poland

³Institute of Fundamental Technological Research, Polish Academy of Sciences, 5B Pawińskiego Str. Warsaw 02-106, Poland

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ABSTRACT: The estimation of degradability of different polyurethanes under natural weather depending conditions in compost pile was the subject of this study. The incubation of polymer samples took place for a period up to 24 months. The characteristic parameters of the compost: temperature, pH, moisture content, and activity of dehydrogenases were monitored and their influence on degradation of polyurethanes was discussed. The compostability of polyurethanes was investigated by changes

of weight, tensile strength, morphology, and thermal properties. The degradation study revealed that the degree of degradation of polyurethanes in the natural environment, like compost, is dependent on their chemical and structural composition. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyurethanes; morphology; thermal properties; degradation; compost

INTRODUCTION

Polyurethanes are an important and versatile class of polymers used in many aspects of modern life. They have found a widespread use in the medical, automotive, and industrial fields and can be found in products such as furniture, coatings, adhesives, construction materials, fibers, paddings, paints, elastomeric parts, and synthetic skins.

Polyurethane is a general term used for a class of polymers which are synthesized from three basic components: a diisocyanate, a polyglycol, and a chain extender. The terminal hydroxyl and isocyanate groups of the substrates allow for alternating blocks, called “segments,” to be inserted into polyurethane chain. Blocks providing rigid crystalline phase and containing isocyanate and a chain extender are referred to as “hard segments.” Those yielding generally either noncrystalline or low crystalline phase and containing polyester/polyether are called as “soft segments.”¹

On the one hand, hard segments contribute to hardness, tensile strength, impact resistance, stiffness, and Young’s 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.

Despite the xenobiotic origins of polyurethanes, they have been found to be susceptible to degradation by naturally occurring microorganisms.

Degradation of polyurethanes is dependent on their properties such as morphology, chemical structure, crystallinity, crosslinking, hard segment to soft segment ratio in the molecular chain etc., which determine the lifecycle of the polymer materials in the environment.^{2–6}

Regarding their possible applications, the degradability of polyurethanes by microorganisms has become an important or even a deciding factor.

The results reported in the literature on polyurethanes degradation mostly come from laboratory studies—in many cases under stable and favorable temperature conditions, providing additional nutrients to microorganisms and using highly concentrated enzymes to promote degradation.^{3,4,6}

The impact of the fungi, bacteria, and enzymes on polyurethane has been tested in different laboratories.^{2,5–9} The degradation of polyurethanes in the laboratory under controlled conditions has been noticed as mainly due to fungal attacks.^{9,10} It is known that polyester-based polyurethanes are much more susceptible to fungal degradation than polyurethanes derived from polyetherdiols.^{9,10}

Correspondence to: K. Krasowska (kraska@am.gdynia.pl).

TABLE I
The Characteristics of Polyurethanes

Polymer	Structure of macrochains	Hard segment (%)
poly(ester-urethane)A	-[PEBA-(MDI-BD) <i>n</i> -MDI] <i>x</i> -	38
poly(ester-urethane)B	-[PCLD-(MDI-BD) <i>n</i> -MDI] <i>x</i> -	38
poly(ether-urea-urethane)	-[PPrO-(MDI-MOCA) <i>n</i> -MDI] <i>x</i> -	48

The degradation of polyurethanes by microorganisms could be due to utilization of polyurethanes as carbon and/or nitrogen sources.¹¹

The aim of this work was the estimation of degradability of different types of polyurethanes in compost under natural weather depending conditions, where those polyurethanes waste could be accumulated.

EXPERIMENTAL

Materials

Three different kinds of polyurethanes were used in this work: poly(ester-urethane)A, poly(ester-urethane)B, and poly(ether-urea-urethane).

The polyurethanes were obtained by two-step condensation reaction.^{12,13} In the first step, the prepolymers were prepared from 4,4'-diphenylmethane diisocyanate/MDI/(Farben Fabriken Byer AG) and different polydiols. The poly(ethylene-butylene-adipate)/PEBA/, $M_W = 2000$ (Zakłady Chemiczne Bydgoszcz, Poland) was used for poly(ester-urethane)A. Poly(caprolactone)diol/PCLD/, $M_W = 2000$ (Interox Chemicals, Great Britain) was used for poly(ester-urethane)B. Poly(propylene oxide)diol/PrO/, $M_W = 2000$ (Nadodrzańskie Zakłady Przemysłu Organicznego "Rokita," Poland) was used for poly(ether-urea-urethane). The molar ratio of NCO : OH was 4 : 1 in all cases in the first step reaction. The synthesis was carried out at 353K.

The prepolymers were further extended by 1,4-butanediol/BD/(BASF, West Germany) to obtain poly(ester-urethane)A and poly(ester-urethane)B or diamine-3,3'-dichloro-4,4'-diphenyl methane /MOCA/ (Gee Lawson Chemicals, Great Britain) to obtain poly(ether-urea-urethane). A chain extender was added to the prepolymer in an appropriate quantity to maintain a steady NCO : OH ratio of 1,1 : 1.¹⁴

The content of hard segments (the reaction product of MDI and low-molecular weight chain extender) in obtained polyurethanes is shown in Table I.

After synthesis the polymers obtained in a form of a sheet (thickness of 2 mm) were cut into dumb-bell shaped samples according to PN-EN ISO Standard¹⁵ and were used for the investigation.

The studied polyurethanes differed not only in their chemical structure but also in their network as well. According to our earlier results of the swelling

test and mass loss for the blind samples of polyurethanes in acetone and THF we can state that poly(ester-urethane)A was uncrosslinked, poly(ester-urethane)B was partially crosslinked by allophanate bonds while poly(ether-urea-urethane) was highly crosslinked by allophanate and biuret bonds. The cryofracture surface analysis confirmed those findings.¹⁴

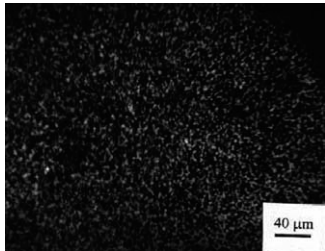

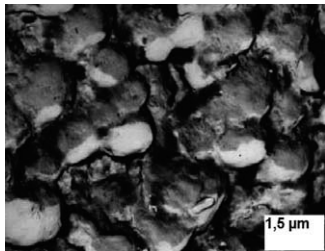
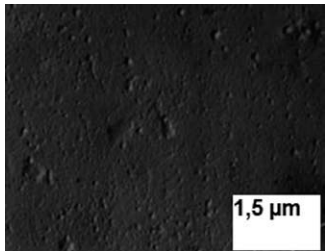
The surface of blind poly(ester-urethane)A was very rough with a very well visible globular microstructure coming from fine crystalline aggregates well visible under reflected optical microscope equipped with polarizer (Table II). The aggregates were present inside the samples as well as they were visible on the fracture surface.¹⁴ The surface view of poly(ester-urethane)A and poly(ester-urethane)B are comparable. However, in case of poly(ester-urethane)A, the amount of crystalline aggregates was higher than in case of poly(ester-urethane)B [compare Table II and Fig. 3(a)]. Contrary to this, no trace of crystalline aggregates was observed in poly(ether-urea-urethane) (Table II). The surface was flat with same microroughness observed under transmission electron microscopy (TEM) and no birefringent elements were observed using optical microscope equipped with polarizer (Table II).

Environment

The degradation of polyurethanes was carried out for up to 24 months, in compost under natural weather depending conditions.

The compost used in this work was formed with the dehydrated sewage sludge taken from 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 kgCaO/1 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 microorganisms growth.

TABLE II
The Microscopic Observations of the Surface of Blind Poly(ester-urethane)A and Poly(ether-urea-urethane)

Poly(ester-urethane)A	Poly(ether-urea-urethane)
<p>I.</p>  <p>Reflected optical microscopy (surface observed with polarizer)</p>	<p>III.</p>  <p>Reflected optical microscopy (surface observed with polarizer)</p>
<p>II.</p>  <p>Electron microscopy</p>	<p>IV.</p>  <p>Electron microscopy</p>

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

Characterization of the compost

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

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

The activity of the dehydrogenases was measured by a spectrophotometric method using triphenyltetrazolium chloride (TTC), which is a method for the estimation of biochemical activity of microorganisms in sludge by using the oxidation process. 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 TF (red compound).¹⁶ Glucose (1.5 g) and TTC (0.2 g) has been added to distilled water (100 mL) and 1 mL of that solution has been added to 5 mL of a compost solution (50 g compost homogenized with 100 mL of distilled water). The final mixture has been incubated at 37°C for 15 min. The dehydrogenation reaction has been stopped by adding ethanol and the intensity of color in the filtered liquid was measured using a Specol colorimeter at 490 nm.

The pH of the compost was determined with a Teleko N 5172 pH-meter. The measurements were done on 50 g samples in 100 mL distilled water after homogenization for 30 min and incubation for 1 h at room temperature.

Investigation of polyurethane samples

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

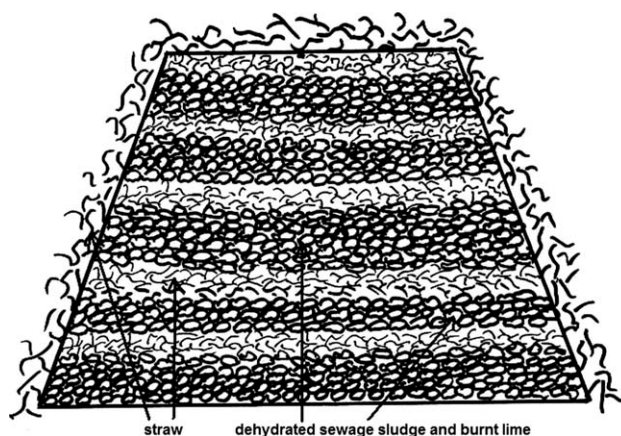


Figure 1 The cross-section of the compost pile prepared in natural environment.

TABLE III
The Characteristic Parameters of the Compost Under Natural Conditions

Month/Year	Parameter			
	Temperature (°C)	pH	Moisture content (%)	Activity of dehydrogenases (mol mg ⁻¹ d.m.)
July	19.0	5.6	54	0,0350
January	6.0	5.3	49	0,0281
July	19.5	5.5	52	0,0328
February	4.0	5.6	50	0,0286
August	22.0	5.4	56	0,0431

The weight, surface morphology, and mechanical properties of polyurethanes were tested before and after incubation in the compost.

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.

Tensile strength (MPa) was measured at room temperature using a Tensile Testing Machine ZMGi-250 according to PN-EN ISO Standard.¹⁵

Microscopic observations of samples surfaces were done at magnification of 1 : 300 using the optical metallographic microscope made by Polish Optical Works with and without polarizers. The pictures were taken before and after incubation in the compost. The surface and fracture surface of blind samples was studied by TEM by replica technique.¹⁷ Two-step replica was prepared using polyvinylalcohol. The replica was shadowed with platinum and covered with carbon.

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 to 230°C in nitrogen atmosphere were recorded.

RESULTS AND DISCUSSION

Degradation environment

It is known that the characteristic parameters of compost such as temperature, pH, moisture content, and activity of dehydrogenases have a significant influence on development of living microorganisms. So, these parameters were monitored during incubation time and their influence on the rate of degradation of polyurethanes is discussed. The characteristic parameters of the compost under natural conditions are presented in Table III.

The data shown in Table III indicate that the temperature had been fluctuating a lot (from 4 to 22°C) during experiment and depended on the weather

conditions. Only the average temperature of compost during summer months (July, August) was on the level preferred for enzymatic degradation, but during the winter months (January, February) the temperature was very low and was not favorable for the biological degradation.

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 in natural compost had been changing a lot and depending on the degree of the growing microorganisms in this environment.

The moisture content of the compost also had been fluctuating a lot. This is due to the weather, as well as to respiration of microorganisms. With decreasing of moisture content lower absolute value of the activity of dehydrogenases was observed.

The pH of the compost was slightly acid (~ 5.5–6). According to the literature, it is known that a wide spectrum of the species of micro- and macro-organisms can exist in compost and the most abundant are bacteria, actinomycetes and fungi.¹⁸ In this study, at rather low temperatures (below 20°C) and slightly acid pH (~ 6) caused that the psychrotrophic acidophilic microorganisms (fungi) could play the main role in the degradation.

Evaluation of the changes of polyurethane samples during environmental degradation

The effects of degradation of polyurethanes in natural compost were evaluated visually at first. Figure 2 represents the surface view at macro scale of all investigated polymers before and after degradation in the compost with activated sludge.

The blind samples of poly(ester-urethane)A were beige and opaque, poly(ester-urethane)B—white and opaque, poly(ether-urea-urethane)—yellow, brownish, and transparent.

The polyurethane samples incubated in the compost were characterized by the flaws at the surface which gradually grew into microcracks, eventually breaking the samples. The surface of poly(ester-urethane)A was scored and cracked. At the end of the experiment, the surface of poly(ester-urethane)B was rough, cracked, and mat with visible black areas. In case of poly(ether-urea-urethane), no significant changes on the surface of incubated samples are seen.

The surface of polyurethanes is observed under the reflected microscope equipped with polarizer before and after degradation (Table II, Figs. 3 and 4).

Microscopic observations after incubation in the compost have shown similar vulnerability of both poly(ester-urethane)A and poly(ester-urethane)B to the microbiological attack. After incubation of poly(ester-

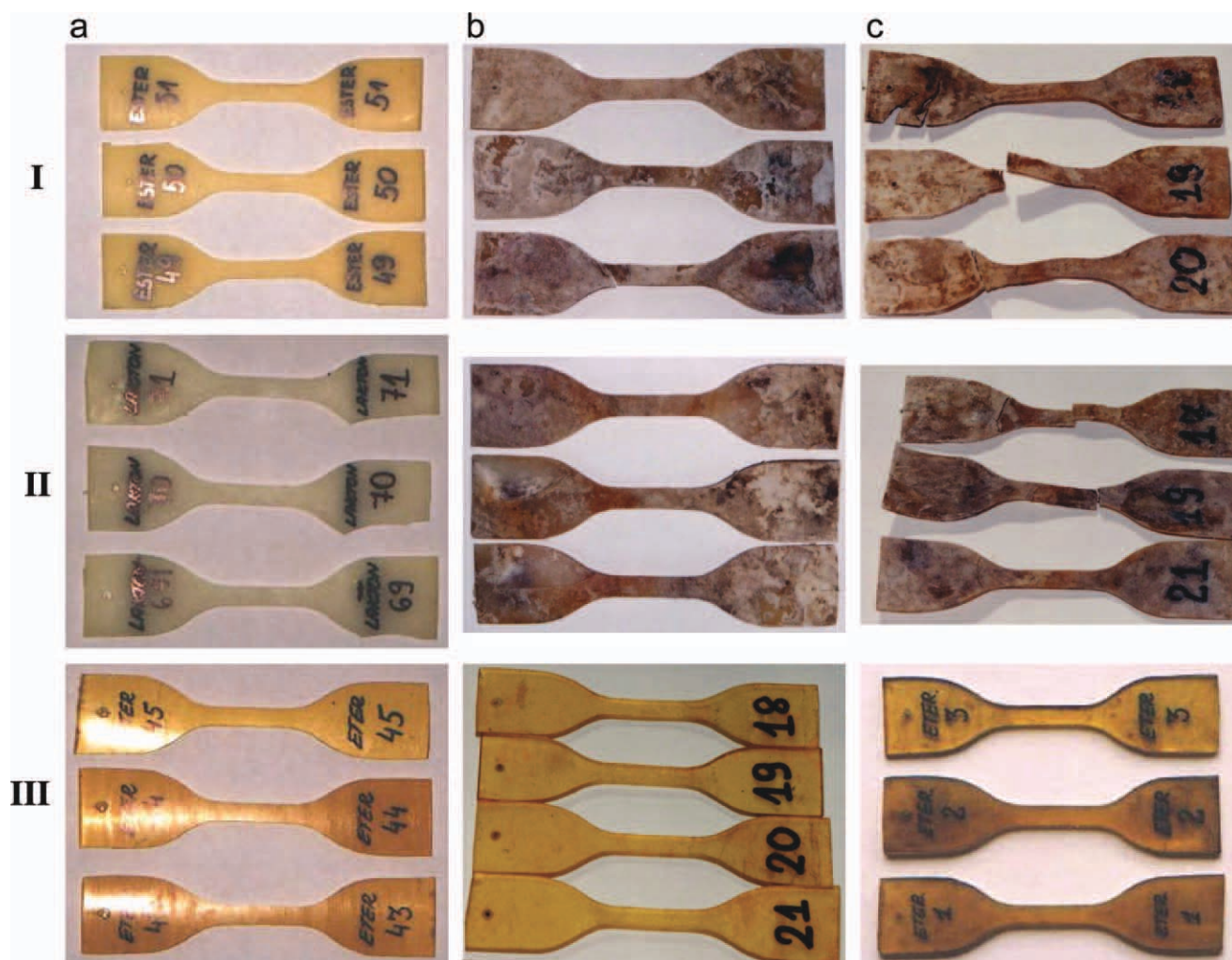


Figure 2 Macroscopic images of the poly(ester-urethane)A [I], poly(ester-urethane)B [II] and poly(ether-urea-urethane) [III] samples: (a) blind sample and after (b) 6 and (c) 12 months of incubation in compost. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

urethane)A and poly(ester-urethane)B in compost, the deterioration of the surfaces has been observed. The changes of surfaces of both polyester-urethanes are comparable. For clarity, only micrographs of poly(ester-urethane)B are presented in Figure 3.

In case of poly(ether-urea-urethane), only very slight changes of the surface have been visible (Fig 4), which suggests the very beginning of deterioration of the samples.

The weight changes of polyurethane samples incubated in the compost are shown in Table IV. Generally, the results presented in Table IV indicate that poly(ester-urethanes) were more vulnerable to microorganisms living in composts than poly(ether-urea-urethane).

The strongest effect of weight loss is observed for poly(ester-urethane)B, despite of being partially cross-linked. It could be mainly explained by degradation of poly(ϵ -caprolactone) in this biotic environment as result of enzymatic hydrolysis of ester bonds suscep-

tible to fungal degradation.^{19–21} This is opposite to results of degradation in sea water,¹⁴ where the conditions were favorable for the development of aerobic epilithic bacteria.

In case of poly(ester-urethane)A, decrease in the mass was on the lower level, than poly(ester-urethane)B, despite of the fact of not being crosslinked.

Considering the parameters of compost (temperature and pH), it could be stated that the psychrotrophic acidophilic microorganisms (fungi) were responsible for the level of degradability of poly(ester-urethanes) based on poly(ϵ -caprolactone).

According to the literature, 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. In the end, hydrolysis rate decreases after the consumption of the amorphous materials by microorganisms.²⁰

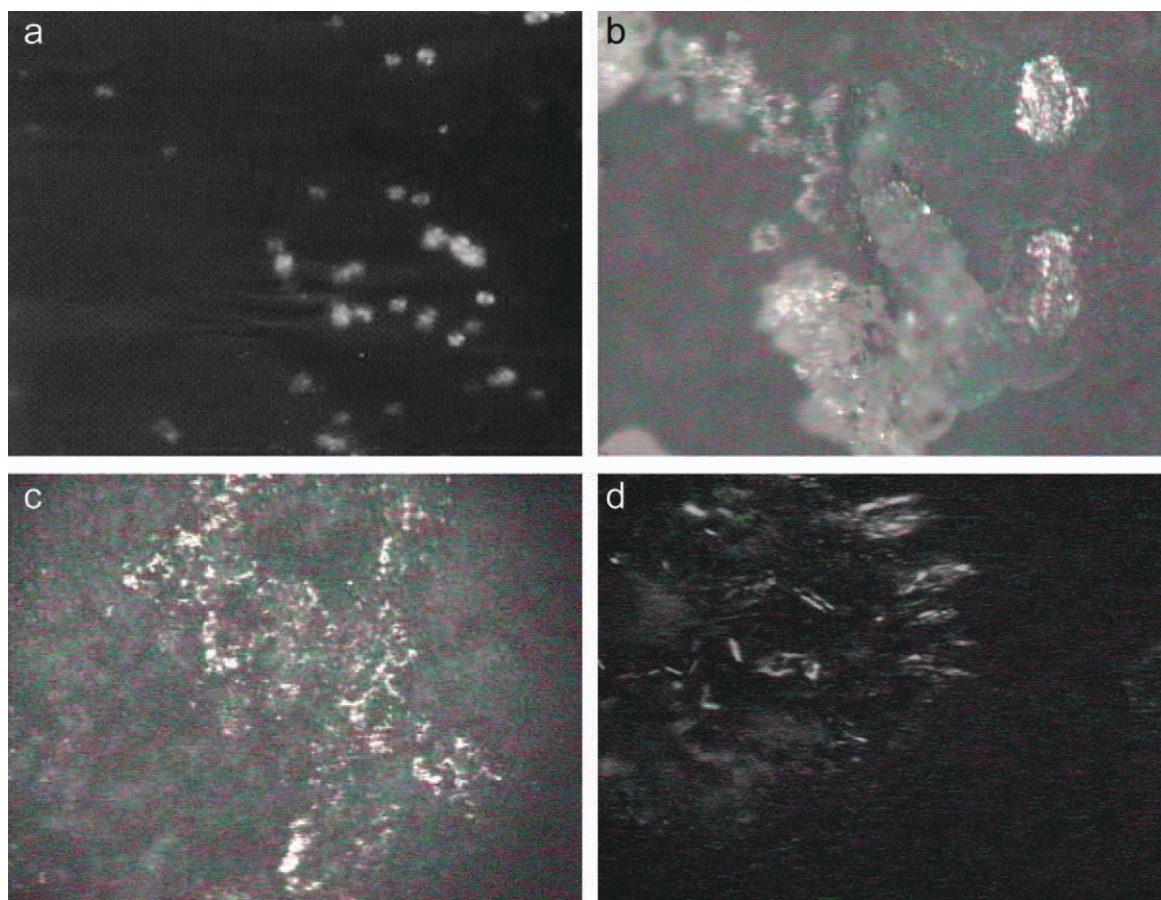


Figure 3 Images of poly(ester-urethane)B observed using reflected optical microscope with polarizer at magnification of 1 : 300 for (a) blind sample and after (b) 6, (c) 12, and (d) 24 months of incubation in compost. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The smallest changes in the mass were observed for samples of poly(ether-urea-urethane). This may be due to high degree of crosslinking as well as to higher resistance of ether than ester structure to microorganism attack.²²

This results also implied that the soft segments are more biodegradable than the hard ones,²³ as it is seen for poly(ether-urea-urethane) with the highest content of the hard segments (48%).

Changes of mechanical properties were checked up by the measurement of tensile strength (σ). The results are presented in Table V.

The rates of the changes of tensile strength (Table V) resemble that of the rate of the mass loss (Table IV); the fastest changes are observed for poly(ester-urethane)B, slower for poly(ester-urethane)A and the slowest for poly(ether-urea-urethane) samples. It is interesting to note, that for blind samples, the highest tensile strength is observed for poly(ester-urethane)B samples, which is due, probably mainly, to being partially crosslinked. As regards the effects of incubation in the compost, important observation is that after 12 months of the treatment, the poly(ester-urethane)-A and -B samples have lost their macro-

scopic intactness breaking into pieces. In case of poly(ether-urea-urethane), samples have kept the intactness. Probably due to high resistance of ether groups to microorganisms attack and crosslinking, the decreases of the tensile strength and elongation with incubation time were very small.

The results of thermal analysis of poly(ester-urethane) samples are shown in Table VI and Figure 5. The DSC analysis of poly(ester-urethanes) revealed the differences in the phase composition (Fig. 5). Generally, both poly(ester-urethanes), -A, and -B, before treatment showed the little presence of crystal phases. Untreated poly(ester-urethane)A contained mainly crystals made of hard segments, which is indicated by small melting peaks at high temperatures [140 and 184°C in Fig. 5(a)]. In case of untreated poly(ester-urethane)B, there is only small melting peak at low temperatures [77°C in Fig. 5b], corresponding to melting of soft segments' crystals.

Due to incubation in the compost, there is an evident increase in crystallinity in both poly(ester-urethanes). However, in case of poly(ester-urethane)A, there appear crystal phases made of both hard and soft segments and in case of poly(ester-urethane)B,

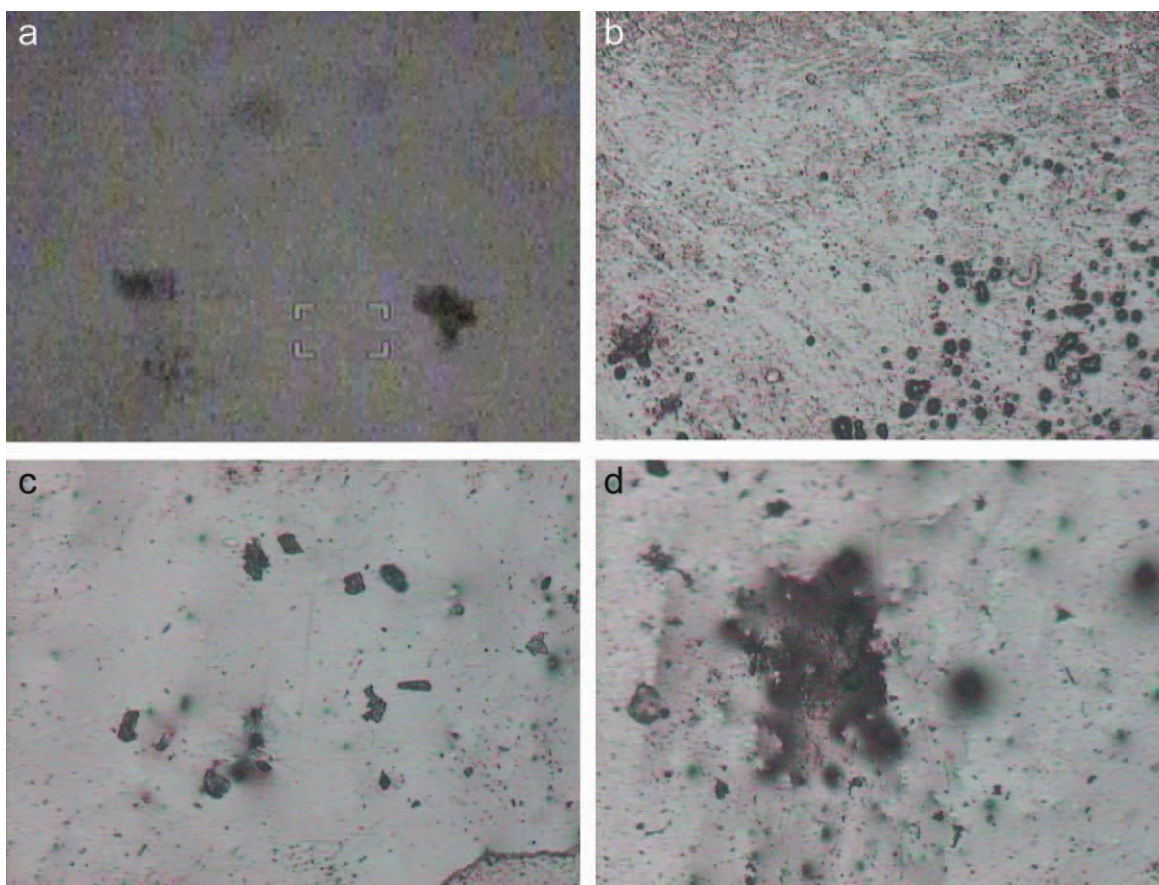


Figure 4 Images of poly(ether-urea-urethane) observed using reflected optical microscope at magnification of 1 : 300 for (a) blind sample and after (b) 6, (c) 12, and (d) 24 months of incubation in compost. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

there appears mainly crystal phase made of soft segments [compare Figs. 5(a,b), and Table VI]. The observation that higher crystallinity develops in poly(ester-urethane)A may be explained by its uncrosslinked structure. In case of poly(ester-urethane)B, the partial crosslinking constrains in some extent of crystallization, especially it seems, of hard segments.

Differences in crystallinity for both poly(ester-urethanes) seem to correspond with mechanical properties results as reinforcing effect of crystal phase is expected. In other words, the smaller decrease in mechanical properties of poly(ester-urethane)A may be due to its higher crystallinity.

TABLE IV
Weight Changes (%) of Polyurethane Samples During Incubation in Compost

Polymer	Incubation time			
	6 months	12 months	18 months	24 months
Poly(ester-urethane)A	-2.1	-4.1	-6.9	-10.7
Poly(ester-urethane)B	-14.0	-19.0	-30.7	-42.9
Poly(ether-urea-urethane)	-0.3	-1.0	-1.1	-1.3

Another issue concerns the behavior at glass transition temperature (T_g) of soft segments. In case of poly(ester-urethane)A, there is no change in position, however, in case of poly(ester-urethane)B, there is a small but an evident shift of T_g to lower temperatures. This observation for the latter poly(ester-urethane) may be due to breaking the crosslinking network, which allows on better phase separation. Moreover, for both poly(ester-urethanes), change in heat capacity at T_g (ΔC_p), may be observed as in agreement with overall melting enthalpy (ΔH). The smaller the ΔC_p , which reflects amorphous phase content, the higher the ΔH reflecting the crystallinity, which is an evidence that amorphous phase degraded first.

TABLE V
The Tensile Strength (MPa) of Polyurethanes Before and After Incubation in Compost

Polymer	Incubation time (months)				
	0	6	12	18	24
Poly(ester-urethane)A	17	8	6	Torn up into the pieces	
Poly(ester-urethane)B	35	4	2	Torn up into the pieces	
Poly(ether-urea-urethane)	20	19	11	11	10

TABLE VI
Glass Transition Temperature (T_g), Change in Heat Capacity at T_g (ΔC_p), Melting Temperature (T_m), and Melting Enthalpy (ΔH) of Crystallites made of Soft (SS) and Hard Segment (HS), Determined From DSC Scans, for Poly(ester-urethane)-A and -B Samples Before and After Incubation in Compost

Poly(ester-urethane)	Incubation time (months)	T_g (°C)	ΔC_p (J/gK)	$T_{m\text{ SS}}$ (°C)	ΔH_{SS} (J/g)	$T_{m\text{ HS}}$ (°C)	ΔH_{HS} (J/g)
A	0	-45	0.317	-	-	140/184	3/3
	6	-45	0.199	48	8	146	39
	12	-51	0.276	51	9	136	2.3
	24	-45	0.236	55	8	151	22
B	0	-46	0.257	77	2.6	-	-
	6	-47	0.267	49	5.5	188	3
	12	-48	0.308	50	3	143/196	2/1
	24	-53	0.202	52	7.6	189	2

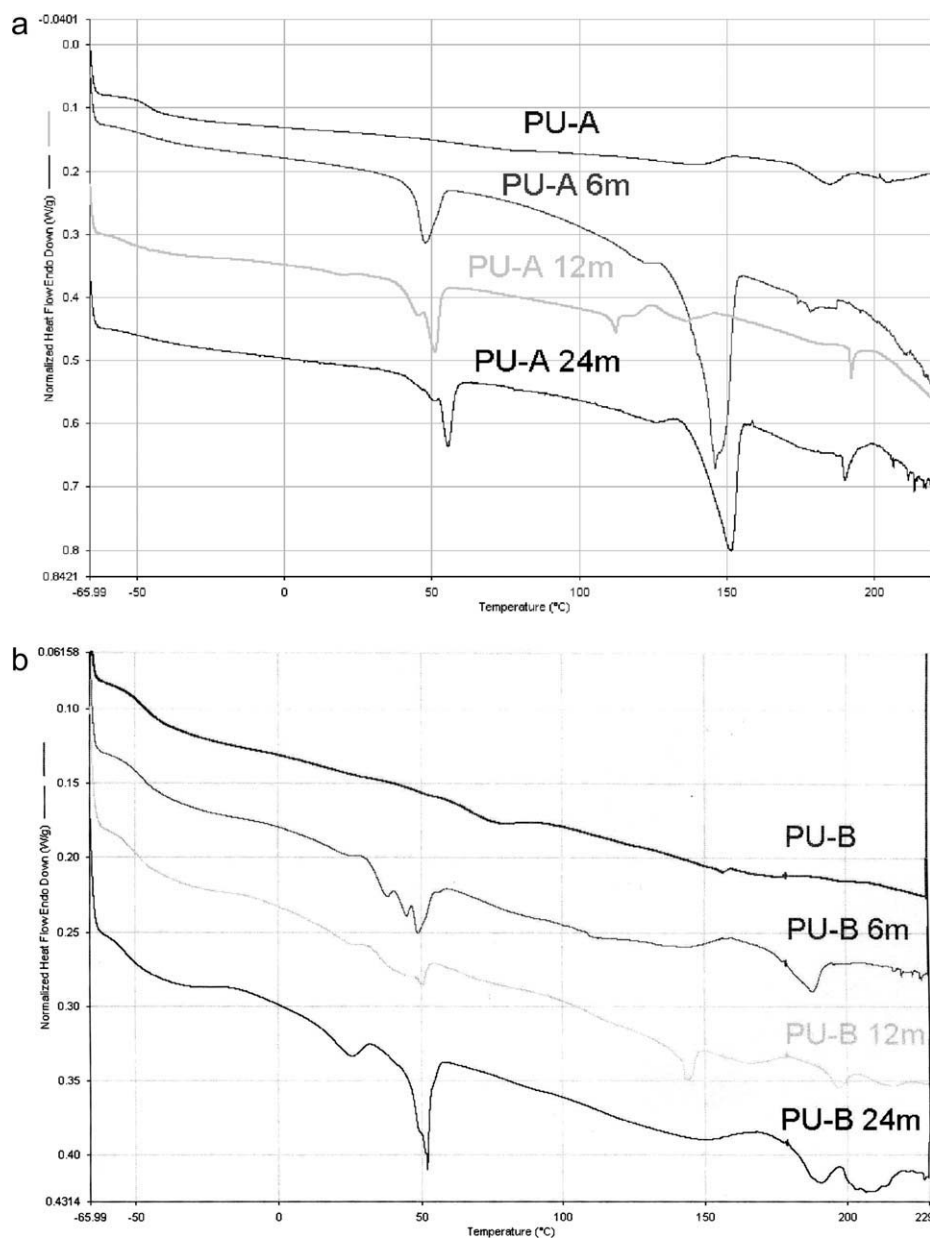


Figure 5 The DSC curves for poly(ester-urethanes): (a) -A and (b) -B before and after incubation in the compost for 6, 12, and 24 months.

CONCLUSION

Process of degradation of polyurethanes was analyzed by monitoring various properties of the samples including weight loss, changes of tensile strength, morphology, and crystallinity. The polyurethanes studied in this work have different degradability in compost under natural conditions. This was due to their susceptibility to fungal attack resulting from differences in chemical structure. The crosslinked poly(ether-urea-urethane) was very resistant to degradation in the compost, while poly(ester-urethanes) were very prone to degradation. Slightly crosslinked poly(ester-urethane)B, based on poly(ϵ -caprolactone) was more vulnerable to degradation in compost, than not being crosslinked poly(ester-urethane)A, based on poly(ethylene-butylene diol)—thus the higher weight losses and deterioration of the surface have been observed. It was because of fragment of poly(ϵ -caprolactone) in the main chain of poly(ester-urethane)B, which is susceptible to microbial degradation in natural environment.

In case of poly(ester-urethanes) the crystallization, as parallel to degradation, was evidenced, leading to appearance of crystals made of hard segments [predominantly in uncrosslinked poly(ester-urethane)A] and made of soft segments [predominantly in partially crosslinked poly(ester-urethane)B].

NOMENCLATURE

σ	Tensile strength
ΔC_p	Change in heat capacity at glass transition temperature
ΔH	Melting enthalpy
BD	1,4-Butanediol
DSC	Differential Scanning Calorimetry
HS	Hard segment
MDI	4,4'Diphenylmethane diisocyanate
MOCA	Diamine-3,3'-dichloro-4,4'-diphenyl methane
PEBA	Poly(ethylene-butylene-adipate)
PCLD	Poly(caprolactone)diol
PrO	Poly(propylene oxide)diol
SS	Soft segment

TEM	Transmission Electron Microscopy
TF	Triphenylformazan
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Melting temperature
TTC	Triphenyltetrazolium chloride

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