

The Influence of Different Processing Additives on Biodegradation of Poly(ϵ -caprolactone)*

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ABSTRACT

The influence of different processing additives on the biodegradation of poly(ϵ -caprolactone) film in the compost with plant treatment active sludge is described in this paper. Poly(ϵ -caprolactone) was incubated for several weeks in compost in natural and laboratory conditions. The characteristic parameters of plant treatment active sludge such as: temperature, pH, moisture content and activity of dehydrogenases and their influence on degradation of poly(ϵ -caprolactone) are presented and discussed. The loss of weight, intrinsic viscosity, tensile strength and morphological changes were tested during the period of degradation. Results of measurement indicate that the biodegradation of poly(ϵ -caprolactone) without additives was very fast in compost with plant treatment active sludge and after six weeks the polymer film was completely assimilated. The introducing of processing additives gives better tensile strength of the materials and less vulnerable to microorganisms attack.

Key Words: biodegradation; enzymatic attack; composting; active sludge, polycaprolactone

INTRODUCTION

Biodegradable plastics have acquired an important place in modern life. Products from biodegradable polymers have been implemented in the medical field, pharmacy, gardening, agriculture and packaging.

Aliphatic polyesters currently constitute the most attractive class of synthetic polymers, which can

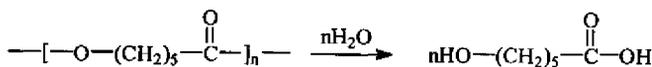
be degraded in contact with living organisms.

According to the literature, degradation of aliphatic polyesters in living environments can result from enzymatic attack or from simple hydrolysis of ester bonds or both (Scheme 1) [1-4].

Poly(ϵ -caprolactone) is an important member of the aliphatic polyester family known as susceptible material to biological degradation, which has been

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Scheme 1. Hydrolysis of poly(ϵ -caprolactone)

confirmed also in our earlier works on biodegradation of poly(ϵ -caprolactone) in different microbially active environments [5–7].

Poly(ϵ -caprolactone) biodegrades whether into the soil or from the attack of special microorganisms; the degradation times vary with the molecular weight, the degree of crystallinity and the morphology [8].

The biodegradation of poly(ϵ -caprolactone) is known to proceed in at least two distinct stages. The first stage of degradation involves non-enzymatic, random chemical hydrolytic ester cleavage autocatalyzed by the carboxyl end groups of polymer chains. The duration of the first stage is determined by the initial molecular weight of polymer as well as its chemical structure. The second stage starts with the slowing down of the rate of chain scission and the beginning of weight loss because of the diffusion of oligomeric species from the bulk. The polymer becomes prone to fragmentation and either enzymatic surface erosion or phagocytosis can contribute to the absorption process [3, 4].

Composting of plastic materials is currently seen as an economical alternative, which can reduce the amount of municipal solid waste.

The compost with plant treatment active sludge is an example of environment where all kinds of micro and macroorganisms, which could be involved in the degradation of polymers, are present.

The general problem of designing biodegradable polymers is the optimization of their chemical, physical processing and mechanical properties as well as their biodegradability.

To improve processing properties some additives incorporated into the polymers are used.

Polymer films have often some inherent problems with friction and adhesion due to the nature of polymer. High friction means that the polymer moves across another surface, causing problems during both the film production and conversion. Whereas film to film adhesion, or blocking can cause

problems during processing and also during end-use (e.g. packaging applications). The most common method of reducing these problems is to add a slip and anti-blocking agent into polymer system. Amides are known to lower blocking and to improve friction. Erucamide and oleamide may function very effectively as slip or anti-blocking additives [9].

The aim of this paper is to examine the influence of different processing additives, performing as a slip or anti-blocking agents, on biodegradation of PCL films in the compost with plant treatment active sludge.

EXPERIMENTAL

Materials

The observations were done on three different samples of poly(ϵ -caprolactone), PCL, with different processing additives. The samples for our studies were kindly supplied by Royal Institute of Technology from Stockholm and they are as follows:

- PCL1 - pure poly(ϵ -caprolactone), trademark Tone 787 with reported molecular weight = 80.000 and ρ (23 °C) = 1.145 g/mL.
- PCL2 - 90% PCL and 10% LE 6471 (ethylene butyl acrylate (EBA) copolymer containing 7% butyl acrylate (BA) with antioxidant) - slip and anti-blocking commercial additive from Neste.
- PCL3 - 90% PCL and 10% OE 5440 (ethylene butyl acrylate (EBA) copolymer containing 17% butyl acrylate (BA) with antioxidant) - slip and anti-blocking commercial additive from Neste.
- PCL4 - 97% PCL and 3% slip masterbatch (LDPE, Erucamide(cis-13-docosenamide), oleamide(cis-9-octadecamide)).

Environments

The incubation of poly(ϵ -caprolactone) took place in the compost with plant treatment active sludge in natural environment and for comparison in laboratory

as well.

The compost pile consisted of active sludge, burnt lime /CaO/(to ravage pathogenic bacterium and eggs of parasites) and straw. It was prepared in natural conditions at sewage farm. The samples of PCL were put into the special basket and buried in the compost pile.

In the laboratory the samples were incubated in compost at the ambient temperature. The incubation lasted for 6 weeks.

Methods

Investigation of Compost Environment

– Dry mass in compost was determined according to Polish Standard [10]. The samples of compost were dried at the temperature 105 °C until a constant weight was obtained. The average samples of approximately 10 g required drying for at least 14 h. When the percentage of the dry mass in compost was known, the moisture content was calculated.

– PH of compost was determined using a pH-meter. To each 50 g sample of compost, 100 mL of distilled water was added. Samples were homogenized for 30 min and put aside for 1 h. The pH of the extract was then measured using pH-meter a Teleko model N 5172f.

– Activity of dehydrogenases (the redox enzyme) was measured by method based on dehydration of glucose added to the compost using "Specol" colorimeter (490 nm) [11].

This is the method for an estimation of biochemical activity of microorganisms in active sludge by oxidation processes of organic compounds.

Investigation of PCL Samples

The changes in weight, the tensile strength, intrinsic viscosity and morphology of poly(ϵ -caprolactone) films were tested during experiment.

– The weight changes (%) were determined using an electronic balance Gibertini E 42s.

The weight of clean and dried samples of PCL after biodegradation was compared with those before biodegradation.

– Intrinsic viscosity of PCL was performed at 25 °C with Ostwald's viscometer. The flow time of 5; 10;

15; 20; 25; 30×10^{-4} [g/dL] solution of polycaprolactone in benzene was determined. The variations of specific viscosity as a function of concentration (c) were extrapolated to $c=0$, and finally the values of intrinsic viscosity were obtained [12].

– Tensile strength of PCL was measured at room temperature using an Instron model 1122 tensile tester. The tensile testing was performed using $150 \times 20 \times 0.04$ mm rectangular strips, in accordance with Polish Standard [13]. The tensile strength was calculated as the tensile force [N] to cross-sectional area [mm²]. The results from three samples were averaged for each value determined.

– Microscopic observations of polymer surface changes were performed at magnification of 1:300 using a PZO metallographic microscope linked with video camera using a programme Software VidPres.

The surface was analyzed before and after biodegradation.

RESULTS AND DISCUSSION

The different conditions in both composts should have an influence on the process of biological degradation of PCL samples. This should be because all parameters of compost (temperature, pH, moisture content and activity of dehydrogenases) have a significant influence on development of living microorganisms in natural environment. Activity of dehydrogenases indicates on variety of microorganisms, which produce enzymes involved in biodegradation process. The absolute value of activity of dehydrogenases is decreasing with decrease in the moisture content of compost, although a fluctuation of pH of environment has a significant influence on activity of dehydrogenases [14].

The characteristic parameters of compost in natural environment are presented in Table 1 and in laboratory condition in Table 2.

Looking at the parameters of both composts (Tables 1 and 2), we have noticed that the higher temperature and moisture content existed in the laboratory, and pH of the compost was on nearing level in natural and laboratory conditions. Whereas, at

Table 1. Parameters of compost in natural environment.

Parameter	Month	
	July	August
Temperature (°C)	18.5	20
pH	5.49	5.17
Moisture content (%)	40.2	33.4
Activity of dehydrogenases (mol/mg d.m.)	0.0318	0.0126

the beginning of the experiment (in July) in natural compost the activity of dehydrogenases was almost twice higher than in August. It could be an effect of different factors (e.g. specific enzymes), which were not analyzed but have influence on biodegradation process.

We had expected, however, that the higher activity of dehydrogenases should have accelerated the degradation process.

Results of weight changes of PCL samples during experiment are shown in Table 3.

The decreases in the weights of all poly(ϵ -caprolactone) samples were observed during all the degradation time in both compost with active sludge.

After two weeks of incubation in the natural environment the weight changes of PCL1, PCL2 and PCL3 are higher than in laboratory compost and even the temperature in the last one was more appropriate for biological degradation [15]. But the absolute value of activity of dehydrogenases was the highest in July in composting natural environment.

Generally, the sample of PCL1 has been degraded most quickly. We have observed the biggest weight loss in natural environment.

PCL2 and PCL3 have been degraded slowly. This could be caused by introducing processing additives into poly(ϵ -caprolactone) system. We have noticed that during two weeks of experiment in compost in natural environment the decrease in weight of PCL3 with EBA copolymer containing 17% BA was higher than in PCL2 with EBA copolymer containing of 7% BA.

The weight changes of PCL4 with 3% slip masterbatch were similar in both composts and higher than in PCL samples with EBA. Probably masterbatch

used as a slip and anti-blocking additive was more preferred by microorganisms living in compost with active sludge. This masterbatch contains organic compounds such as: Erucamide (usually derived from vegetable oils) and oleamide from animal fats. Microorganisms utilize these amides or another simple nitric forms such as: ammonium, nitrate, and nitrite to build their own proteins.

In the second month the parameters of the compost in laboratory such as the temperature, pH, activity of dehydrogenases and moisture content were higher than in natural term. But even that the changes of weight of PCL samples incubated in this compost after four weeks were smaller. In the natural environment the changes of weight were so significant, that the fragmentation occurred very early and then enzymatic surface erosion started quickly.

After four weeks of experiment in natural condition we could also observe that the introducing of 10% EBA copolymer containing of 7% butyl acrylate into polycaprolactone slows down biodegradation more than the adding of 10% EBA copolymer containing of 17% butyl acrylate or 3% slip masterbatch containing LDPE. This is because of higher content of polyethylene segments in EBA copolymer containing of 7% BA. It is known that polyethylene is very resistant in microbially active environments and mainly an oxidation process is an important degradation step for polyethylene [16].

By observing the results of weight changes we could make the assumption that the masterbatch is assimilated easier by microorganisms living in natural conditions than ethylene butyl acrylate.

After six weeks of incubation in composts all poly(ϵ -caprolactone) samples almost lost their weight.

Table 2. Parameters of compost in laboratory.

Parameter	Month	
	July	August
Temperature (°C)	23.5	24.5
pH	5.48	5.24
Moisture content (%)	52.8	46.3
Activity of dehydrogenases (mol/mg d.m.)	0.0189	0.0153

Table 3. Weight loss (%) of PCL after incubation in composts with active sludge.

Environment		Incubation time (weeks)		
		2	4	6
PCL1	compost in natural environment	-25.24	-88.86	destroyed
	compost in laboratory	-6.22	-22.73	-88.36
PCL2	compost in natural environment	-3.25	-14.61	-88.54
	compost in laboratory	-2.5	-4.33	-61.60
PCL3	compost in natural environment	-5.74	-16.17	-84.22
	compost in laboratory	-1.9	-25.21	-72.75
PCL4	compost in natural environment	-5.9	-18.83	-91.38
	compost in laboratory	-6.0	-13.52	-69.76

However, the presence of processing additives made the degradation process weaker. Slip additives by migrating to the polymer surface and forming monolayer or multi-layers on the surface and in this way the enzymatic attack on ester group is postponed. The effect of introducing slip and anti-blocking commercial additive into poly(ϵ -caprolactone) on the degradation process has only the physical characteristic effect.

The changes of intrinsic viscosity of poly(ϵ -caprolactone) after degradation are giving indications about changes of molecular weight. The characteristic parameters are shown in Table 4. The longer the incubation time in the compost with active sludge the higher decrease of intrinsic viscosity of biodegraded pure PCL. This could be the result of decrease in molecular weight of PCL. The changes in molecular weight were less significant for PCL with additives - especially in first two weeks. From the data we could also state that the presence of processing additives

postpones the biodegradation of poly(ϵ -caprolactone). The observed changes of intrinsic viscosity of poly(ϵ -caprolactone) degraded in compost and in laboratory confirmed the results of weight changes.

It has been known that processing additives make easier technological processes and they produce excellent results during end-use, for example reducing friction and adhesion in packaging applications [9]. We could expect that they have also an influence on mechanical properties. Results of tensile strength of PCL samples before biodegradation are shown in Table 5.

The obtained results indicate that the incorporating of different processing additives into the system improves the tensile strength. The tensile strength of PCL samples was measured only before degradation process because after two weeks incubation in compost with active sludge the samples were almost cut up into pieces.

Table 4. The intrinsic viscosity (dL/g) of PCL incubated in composts with active sludge.

Environment		Incubation time (weeks)			
		0	2	4	6
PCL1	compost in natural environment	1.04	0.53	0.36	-
	compost in laboratory		1.06	0.91	0.30
PCL2	compost in natural environment	1.08	0.87	0.52	-
	compost in laboratory		0.76	0.69	0.40
PCL3	compost in natural environment	0.89	1.12	0.80	-
	compost in laboratory		1.06	0.71	0.49
PCL4	compost in natural environment	1.03	0.77	0.61	-
	compost in laboratory		0.64	0.78	0.67

Table 5. Tensile strength (MPa) of PCL blank samples.

Tensile strength (MPa)	PCL1	PCL2	PCL3	PCL4
	19.5	23.7	20.2	21.2

The samples of poly(ϵ -caprolactone) were also observed under metallographic microscope before and after biodegradation with and without polarizers. Microscopical observations have shown deterioration of poly(ϵ -caprolactone) surface (Table 6).

The surface of pure PCL was a fine-aggregates and birefringent. Introduction of processing additives into the poly(ϵ -caprolactone) system makes the surface more or less orientated.

After two weeks of biodegradation in compost with active sludge in natural environment we observed the increase of birefringent elements, which could be an evidence for crystallinity increase. This confirms that amorphous phase was attacked first. After four weeks of experiment the crystalline phase was becoming less visible (less orientated birefringent elements). After six weeks we could see very distinctly the black area, which could be non-birefringent part of the sample after an attack and an agglomeration of microorganisms.

CONCLUSION

Biodegradation of PCL, poly(ϵ -caprolactone), without additives is very fast in microbially active environments. The film was assimilated completely over the period of six weeks. This means that polycaprolactone is very sensitive to an enzymatic attack of microorganisms in living environments.

The obtained results indicate that the incorporation of processing additives such as: slip and anti-block agents into the poly(ϵ -caprolactone) system on the one hand gives better tensile strength of the material and in this way could create the new possibilities of uses in the gardening, agriculture, and packaging. On the other hand, those polymers are less vulnerable to microorganisms attack, but still they can degrade in contact with living organisms. The kinetics of biodegradation, however, is influenced by the kind of processing compounds.

The changes in weight and microscopical observations after incubation of poly(ϵ -caprolactone) with processing additives in the compost with active sludge confirm the conclusion that the biodegradation of poly(ϵ -caprolactone) system occurs in two stages [3, 4]. In the first stage of degradation, which is

Table 6. Microscopic surface observations under metallographic microscope of the samples kept in natural environment.

Time (weeks)	PCL1	PCL2	PCL3	PCL4
0	fine-aggregates, birefringent	fine-aggregates, very strongly orientated, birefringent	fine-aggregates, very slightly orientated, birefringent	very fine-aggregates and slightly orientated, birefringent
2	increase of birefringent elements, slight cracks on the surface with small dark areas	more birefringent and less orientated	birefringent and the decay of orientation	increase of birefringent elements appearance of black areas
4	less birefringent, strong cracks	non-birefringent, the further decay of orientation, small cracks	the decay of birefringence and orientation	the decay of birefringent elements appearance of microcracks
6	destroyed	very distinct black areas which represent an agglomeration of microorganisms and holes	similar to PCL2 + slightly small birefringent areas	very distinct black areas which represent an agglomeration of microorganisms

non-enzymatic hydrolysis, we observed the less changes in weight and in the surface than the second stage of enzymatic degradation.

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