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Biodegradation of polycaprolactone in plant treatment active sludge

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SUMMARY: The object of this study was the degradation of polycaprolactone films in a living composting environment with plant treatment active sludge. The incubation of polymer samples took place in the compost for a period up to 3 months. There are presented the characteristic parameters of plant treatment active sludge: temperature, pH, dry mass and activity of dehydrogenesis and their influence on degradation of polycaprolactone is discussed. The changes of weight, tensile strength, microhardness and morphology during experiment were tested. Enzymatic activity is resulted in surface erosion. Microscopical observations show deterioration of polycaprolactone surface. Hydrolysis („bulk process") is also contributed (onset of weight loss). The decreasing of weight and mechanical properties are observed after each period of incubation. The increase in the microhardness during first period of biodegradation can be directly proportional to the increase in crystallinity, because amorphous regions are degraded first what is confirmed by microscopical observation. The complete degradation of polycaprolactone in compost with plant treatment active sludge in living environment takes place after short period of time (3 month).

Introduction

The increasing usage of polymers in disposable items as packages creates increasing problems of garbage disposal and demands for their degradation. Aliphatic polyesters currently constitute the most attractive class of artificial polymers which can get degraded in contact with living organisms. Polycaprolactone is an important member of the aliphatic polyester family, known to be susceptible to biological degradation. It is investigated mainly in the context of application in drug delivery systems and packaging materials. There are literature reports on degradation of aliphatic polyesters in a living environment. This degradation can result from enzymatic attack or from simple hydrolysis of ester bonds or both[1]. The degradation rate depends on moisture level, nutrient supply, temperature and pH[2]. In this paper we describe the results of biological degradation of polycaprolactone films in a living composting environment with plant treatment active sludge.

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Experimental

Materials:

Four samples (PCL F1, PCL F2, PCL F3, PCL F4) of polycaprolactone (MW = 80 000, density ρ (23°C) = 1.145 g/cm^3) with different processing additives were investigated.

Environment:

The incubation of polymer samples took place in compost with plant treatment active sludge in living environment for a period up to 3 months. The characteristic parameters of plant treatment active sludge are presented in Tab. 1.

Tab. 1. Parameters of plant treatment sludge

Parameter	October	November	December
Temperature [^{0}C]	15	12	8
pH	5.11	5.31	5.53
Dry mass [%]	60.75	65.32	59.25
Activity of dehydrogenesis [μmol/mg s.m]	1.73	1.80	1.12

Methods:

The weight changes, tensile strength, microhardness and morphological changes during experiment were tested.

Weight changes (%) were determined by means of an electronic balance Gibertini E 42s.

Tensile strength was measured by means of Instron 1122.

Microhardness was investigated at room temperature using Shimadzu Dynamic Ultra - Microhardness tester. The test used a squared pyramidal diamond intender.

Polymer surface changes were observed under optical microscope at magnification of 1 : 300.

Results and discussion

The parameters of plant treatment active sludge are presented in Table 1. Temperature is a critical factor in chemistry and thus it plays an important role in polymer degradation where the rate increases with temperature[3]. A great majority of „in vitro" experiments were realised at 37°C. In our experiment the temperature was relatively low (varying from 15°C to 8°C).

According to the literature[1] we can reasonably conclude that alkaline and strong acid do media accelerate polymer degradation, but major difference is found between the slightly acidic and neutral media. In our experiment there was no significant difference observed in pH (pH varying from 5.11 to 5.33). The contents of dry mass in compost also did not change distinctly. Even though the activity of dehydrogenesis - which depends on pH, moisture level and temperature - was highest in November and thus favourable for biodegradation of polycaprolactone, because the symptoms of degradation are clearly observed.

Enzymatic activity resulted in surface erosion - although hydrolysis („bulk process") occurs as well (onset of weight loss)[1]. The weight losses of investigated polycaprolactone samples incubated in compost with plant treatment active sludge are shown in Tab. 2. The weight decrease of all polycaprolactone samples is observed after incubation. PCL F1 and PCL F4 show bigger weight loss than PCL F2 and PCL F3, and after 12 weeks of biodegradation the samples are destroyed completely.

Tab. 2. Weight loss [%] after incubation of PCL samples in plant treatment sludge

Polymer	Incubation time (weeks)			
	2	4	8	12
PCL F1	- 2.08	- 19.03	-	destroyed
PCL F2	- 1.30	- 7.03	- 17.45	- 20.28
PCL F3	- 1.63	- 9.45	- 43.40	- 49.20
PCL F4	- 1.73	- 46.9	-	destroyed

Changes of mechanical properties such as tensile strength are shown in Tab. 3. The tensile strengths of PCL F1 and PCL F4 are also decreasing faster and after one month of biodegradation this measurement was impossible to be undertaken.

Tab. 3. Tensile strength R [MPa] of PCL samples after incubation in plant treatment sludge

Polymer	Incubation time (weeks)		
	0	2	4
PCL F1	31.9	18.3	-
PCL F2	37.5	25.9	5.4
PCL F3	21.7	18.3	3.8
PCL F4	24.8	20.0	-

Polymer morphology (semicrystallinity) plays a critical role in degradation phenomena. It is known that degradation of semicrystalline polymers occurs in two stages. The first stage consists of water diffusion into the amorphous regions with random hydrolytic scission of ester bonds. Then the hydrolytic attack progresses within crystalline domains[4].

Microscopical observations of investigated polycaprolactones revealed surface deterioration (Fig.1). After 2 - 4 weeks of biodegradation in the plant treatment sludge we could observe the increase of orientated birefringent elements, what could be as an evidence of increase in crystallinity. It has confirms that amorphous regions are degraded first. It is confirmed by microhardness results. The kinetics of changes is different for every investigated polycaprolactone.

Microhardness has emerged in recent years as a physical method which can offer a direct information on changes in morphology. The increase in the microhardness of polycaprolactone during the first period of biodegradation can be directly proportional to the increase in crystallinity (Fig.2). It is attributed to crystallization of the tie segments made possible by chain cleavage in the amorphous phase facilitated by the glass transition temperature of polycaprolactone. Microhardness increase has confirmed that amorphous regions are degraded first. The first stage of degradation (2-4 weeks) involves nonenzymatic random hydrolytic ester cleavage, autocatalysed by carbonyl end groups of polymer chains. The second stage starts with the slowing down of the rate of chain scission and the beginning of weight loss (after 1 month) because prone to fragmentation and either enzymatic surface erosion or phagocystosis contribute to the absorption process[5].

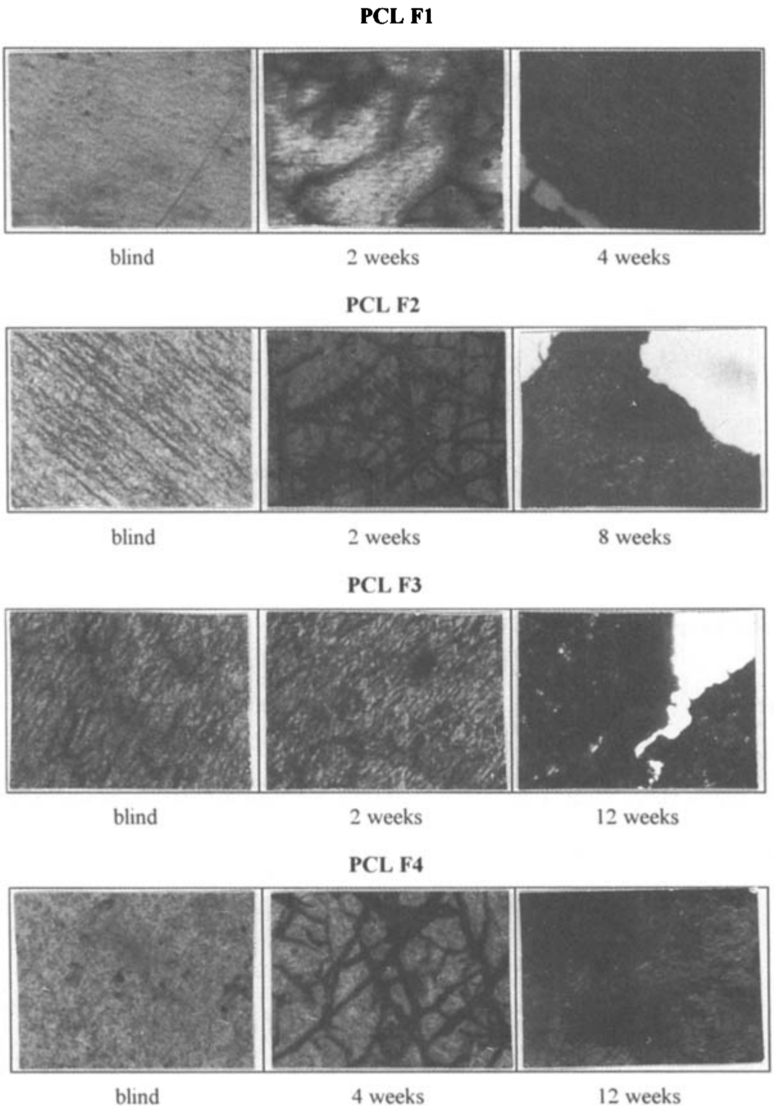

Fig. 1. The surface of PCL samples before degradation (blind) and after incubation in plant treatment sludge, scale 40μm

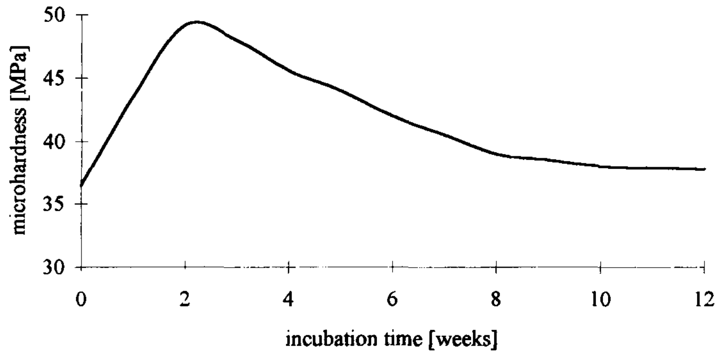

Fig.2.Changes in microhardness of PCL F3 samples after incubation in plant treatment sludge

In conclusion we can state that degradation of polycaprolactone in compost with plant treatment active sludge in living environment takes place very quickly and even can be controlled by special conditions of environment.

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