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Biodegradation of plastic bottles made from 'Biopol' in an aquatic ecosystem under *in situ* conditions

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Abstract

Experiments have been carried out in Lake Lugano, Switzerland, in order to study the biodegradation of poly(3-hydroxyalkanoates) (PHA) in an aquatic ecosystem under natural conditions. Commercially available plastic articles made from PHA, such as bottles and films, were incubated for 254 days in a water depth of 85 m. Shampoo bottles were positioned precisely on the sediment surface by the use of a small manned submarine. A set of bottles was attached to a buoy in order to incubate plastic material in different water depths. When incubated in the water column or on the sediment surface, a life span of five to ten years for this specific bottle type was calculated. *In situ* degradation rates of 10 to 20 mg/d were determined. PHA films were completely degraded when incubated in the top 20 cm of the sediment. The results clearly demonstrate that in an aquatic ecosystem (water column as well as sediment) under *in situ* conditions (i.e. low temperatures, seasonal variations of the oxygen concentration) plastic goods made from PHA are degraded.

Introduction

According to a recent survey (Rogers 1990), 72% of the American people regarded plastics among solid waste materials as the greatest threat to the environment mainly because plastic articles are not biodegradable. In order to react to the legislative pressure to ban plastic packaging, the plastic industry has been forced to intensify the efforts in developing efficient recycling processes as well as biodegradable materials.

Recently, industrial interest has been focussed on microbially produced poly(3-hydroxyalkanoates), PHA, for use as natural, biodegradable, and biocompatible thermoplastics with a wide range of potential applications (Brandl et al. 1990; Holmes 1985; Howells 1982; King 1982; Uttley 1986).

PHA is a naturally occurring storage polyester formed by a very broad range of microorganisms (Brandl et al. 1990; Steinbüchel 1991). Poly(3-hydroxybutyrate), PHB, is the most known representative of the family of PHA. PHA is now being produced industrially, on a fairly large scale, by ICI Ltd. in Great Britain. The polymeric material (a 3-hydroxybutyrate/3-hydroxyvalerate copolymer) is commercially available under the trade name BIOPOL® and can be used as a raw material for the production of commodity plastics by traditional processing techniques such as injection molding, extrusion, blow molding, melt casting, or spinning (Byrom 1987; Mann & Calvert 1987; Uttley 1986).

PHB homopolymer shows similarities in its physical properties and even in its molecular structure to the isotactic polypropylene (Bloembergen 1987). The main difference, however, is the bio-

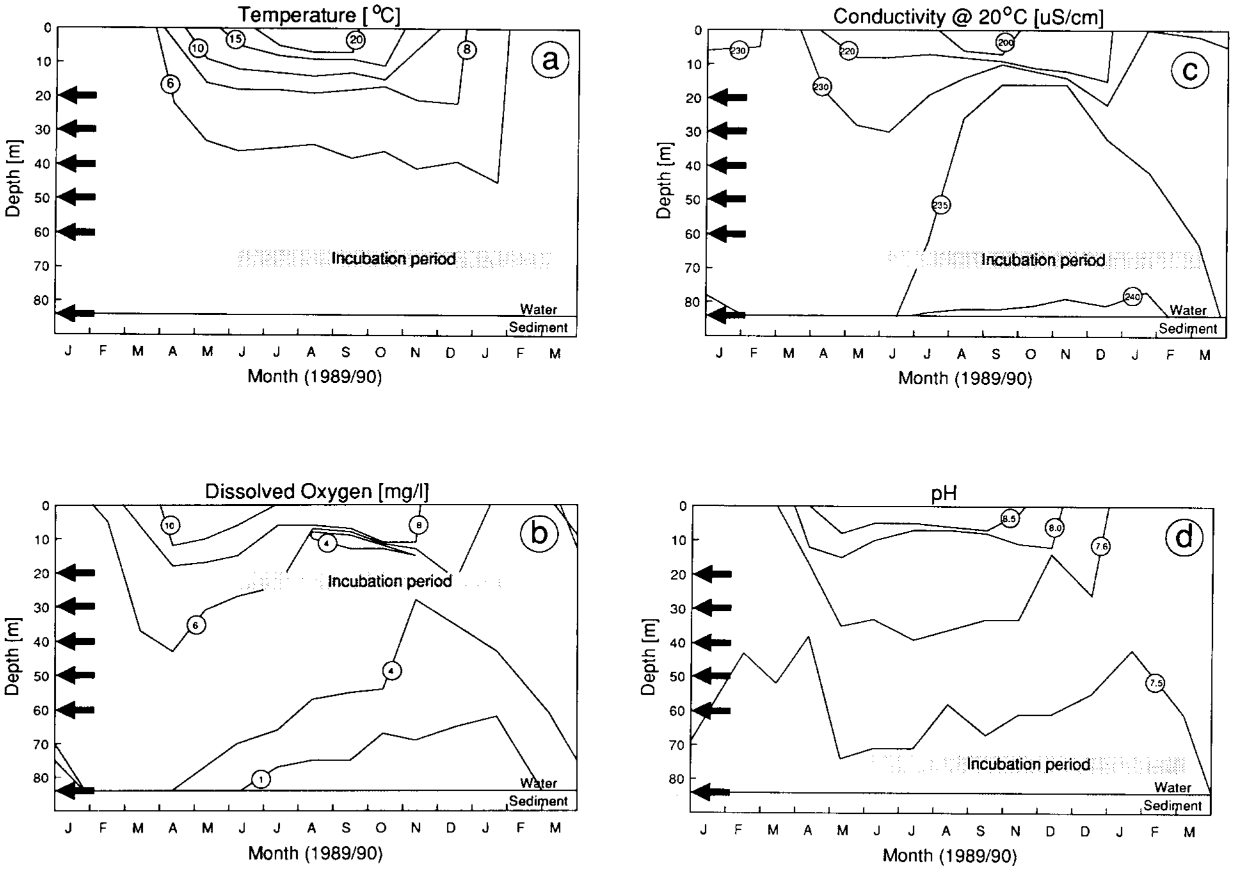


Fig. 1. Physical and chemical paramaters of Lake Lugano during the experimental period of 1989/90. a: temperature (°C); b: dissolved oxygen (mg/l); c: conductivity at 20 °C (μS/cm); d: pH. Arrows indicate the different incubation depths of the plastic bottles. Bars represent the incubation time.

degradability of PHB compared to the insignificant degradation of polypropylene. A further difference, which might be important in its practical application, is the density of PHB in comparison to other plastic materials. Because of its high density, PHB does not float in an aquatic ecosystem. Therefore, once discarded, plastic goods made from PHB will sink and will be degraded in the surface sediments by biogeochemical mechanisms.

In general, a series of parameters can influence the rate of biodegradation and the life time of a plastic material in nature, including the type of environment, the presence of a microbial population and its microbial activity, the availability of water, the temperature, the section thickness of the plastic material, its surface texture, its porosity, and the presence of second components in the plastic, such as fillers or coloring agents.

Here we report on *in situ* experiments in order to study the biodegradation of bottles and films made from PHA in a natural aquatic ecosystem. The objectives of this study were: (i) to investigate the degradability of commodity plastic articles made from PHA in the water column as well as in the surface sediments; (ii) to determine quantitatively life span and degradation rates of the specific plastic goods under natural conditions.

Materials and methods

Our study was carried out on the sediment surface

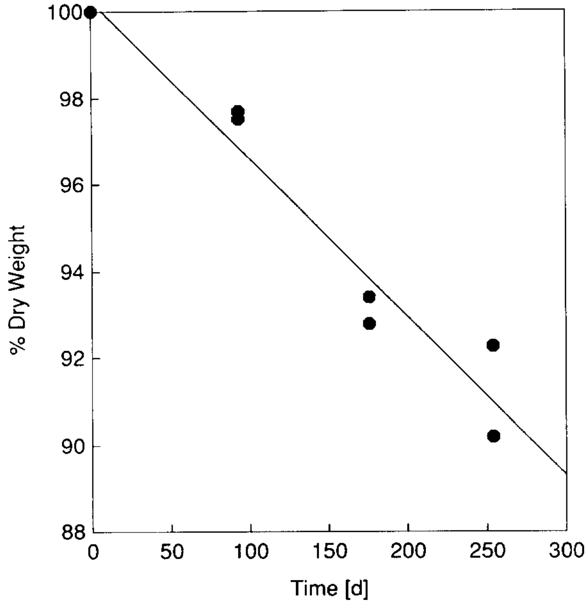


Fig. 2. The degradation of bottles made from BIOPOL® in the surface sediments of Lake Lugano, Switzerland, in a water depth of 85 m. Degradation was measured as weight loss after retrieval of the bottles.

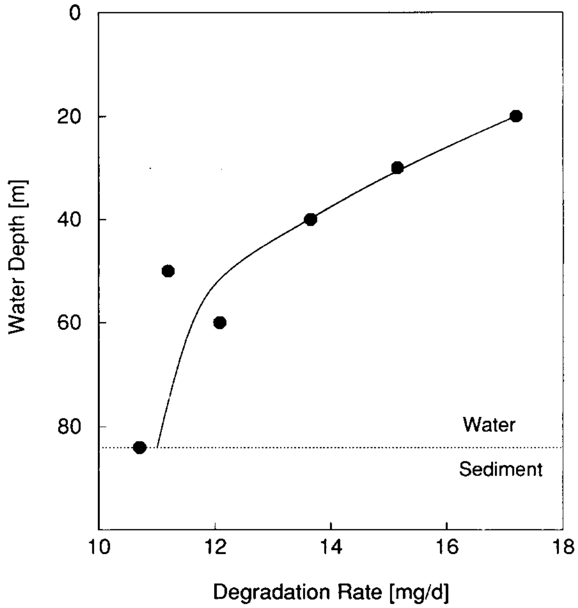


Fig. 3. Degradation rates of bottles made from BIOPOL® as a function of water depth. The bottles were incubated in Lake Lugano, Switzerland, for 260 days. Degradation was measured as weight loss after retrieval of the bottles.

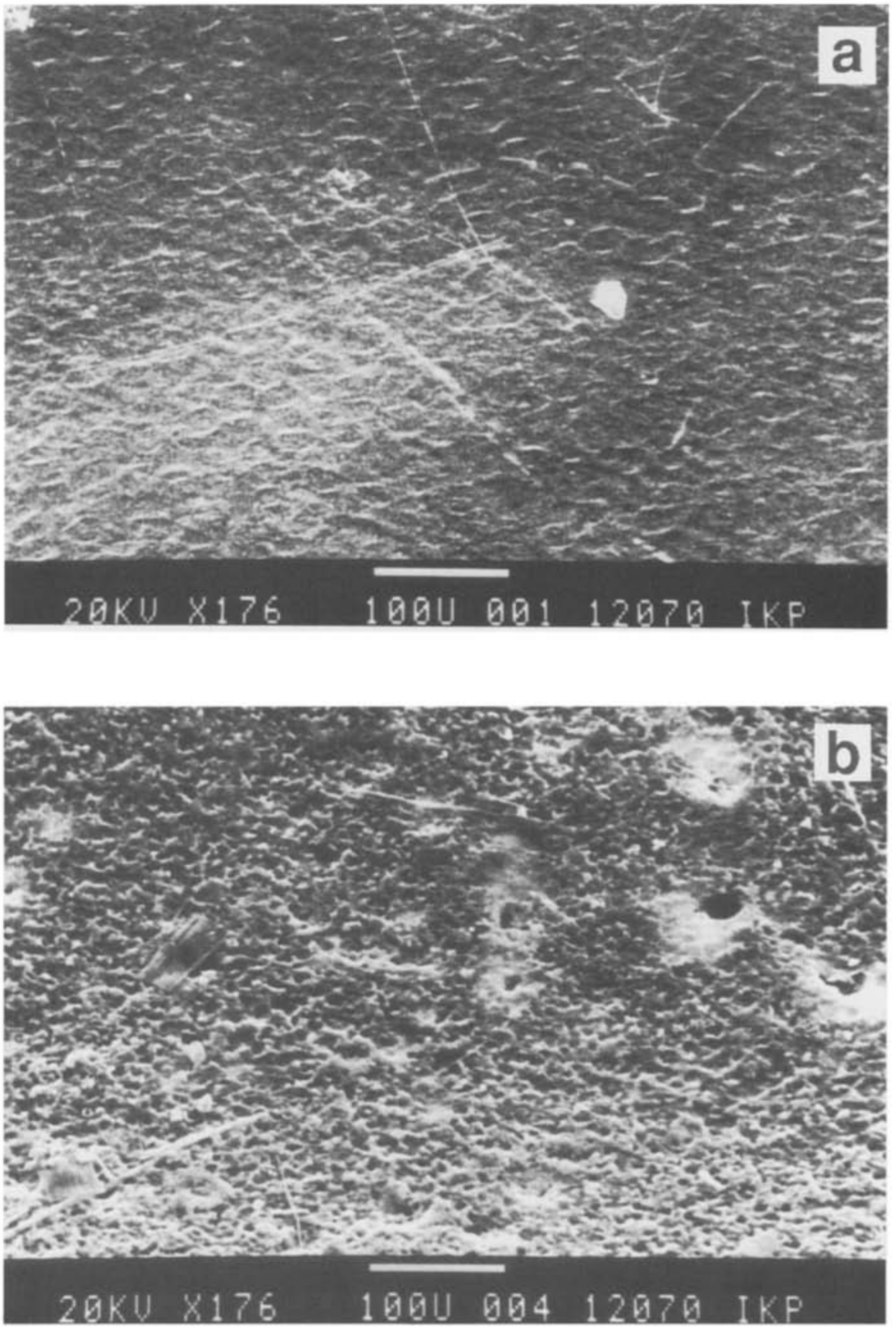
of Lake Lugano, Switzerland, outside of Melide in a water depth of 85 m. Lake Lugano is a highly eutrophic aquatic ecosystem. During stratification of the lake the hypolimetic water becomes anoxic at the experimental site (Fig. 1). In order to determine the environmental conditions influencing the degradation rate, certain physical and chemical parameters such as temperature, oxygen concentration, conductivity, and pH were monitored monthly by the use of a winch-operated multiparameter probe (Idronaut, Milano, Italy).

All experiment bottles were positioned and retrieved by the manned submarine 'F.-A. Forel'. For incubation experiments on the sediment surface, PHA bottles were mounted horizontally on PVC tubes. The tubes were implanted in the sediments with the aid of the hydroelectrical manipulation arm of the submarine in such a manner that they were positioned precisely at the sediment-water interface. A set of bottles was attached to a buoy in order to incubate plastic material in different water depths (20, 30, 40, 50, and 60 m, respectively). Bottles from the sediment surface were retrieved after 93, 176, and 254 days, respectively. The buoy with the suspended bottles was retrieved after 260 days. The extent of degradation was determined gravimetrically as weight loss and the life span (time for a 100% weight loss) as well as the degradation rates were calculated.

The bottles were made available by Wella AG (Darmstadt, Germany) and consisted of a PHA copolymer with a molecular composition of 92% 3-hydroxybutyrate and 8% 3-hydroxyvalerate, approximately 9% triacetin, and approximately 1% boron nitride. The average weight was 31.90 g (n = 13). The outer and inner surface area was 356 and 336 cm^2, respectively.

As control, two bottles were washed with ethanol and stored in autoclaved water at 4 °C in the laboratory for 234 days. The weight losses of the control bottles were taken into account when determining the degradation of the bottles from the *in situ* experiments.

For degradation studies in the lake sediment, glass slides were wrapped with PHA film (thickness 17 μm). The slides were mounted on a rack



which was vertically implanted in the sediment so that the PHA film was positioned in different sediment layers as well as in the supernatant water. An identical rack with slides wrapped with Saranex, a polyethylene based material which is not degradable under these conditions served as control (Brandl & Hanselmann 1991). The racks were incubated for 254 days. After incubation, very small pieces of film material could be recovered from the glass slides. The pieces of film were fixed with glutaraldehyde immediately after retrieval of the incubation rack. The extent of degradation was observed by scanning electron microscopy.

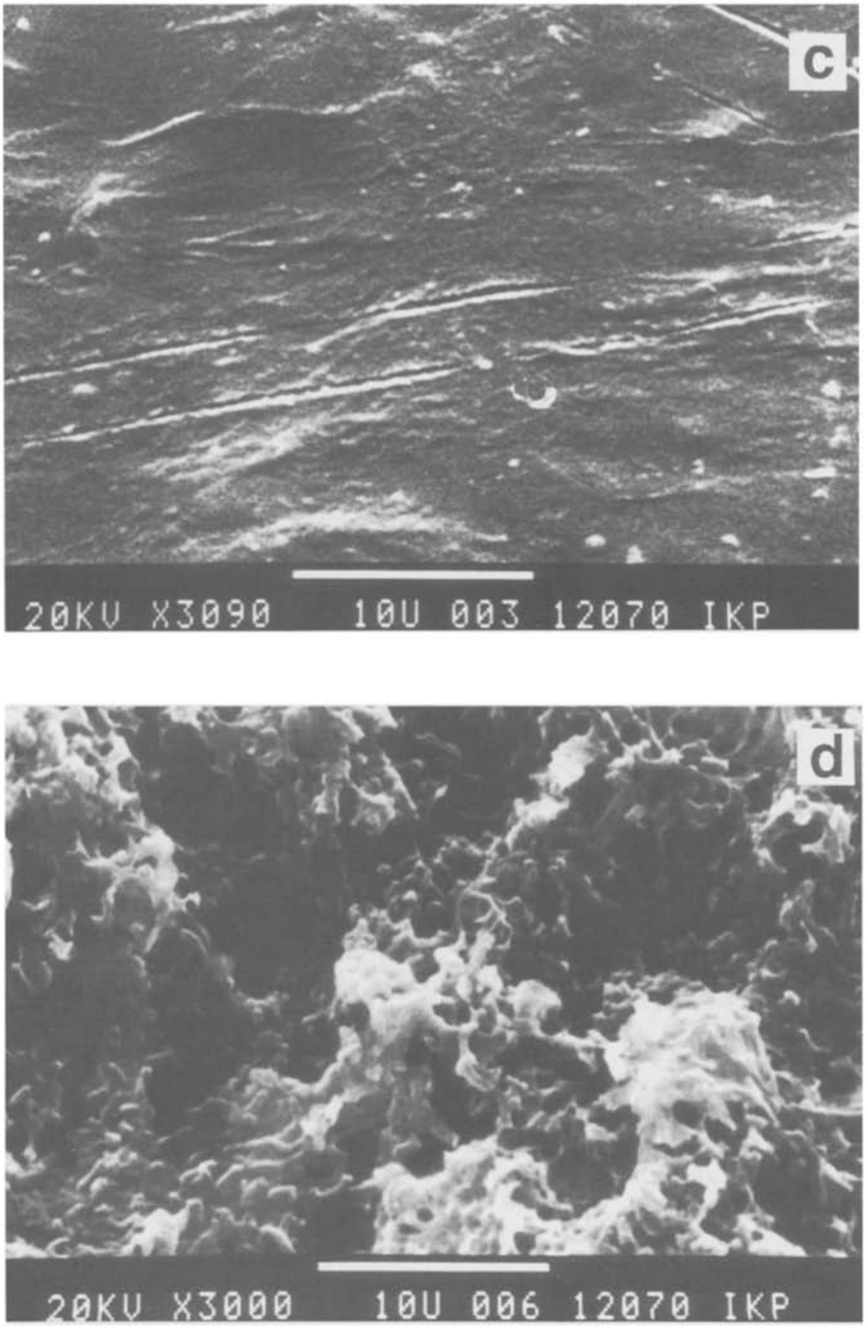


Fig. 4. SEM photographs of the surface of Biopol® film exposed to lake sediments. Films were incubated for 260 days in the anoxic sediment of Lake Lugano in a water depth of 85 m. a: The surface of the film before incubation at low magnification (176x). b: after incubation at low magnification (176x). c: before incubation at high magnification (3000x). d: after incubation at high magnification (3000x). (Photographs were taken by G. Fischer, IKP, University of Stuttgart, Germany).

Results

Data on the environmental conditions (temperature, dissolved oxygen, conductivity, pH) prevailing during the experimental period are presented in Fig. 1. Most of the incubation time the water column was stratified (Fig. 1a) providing therefore relatively stable environmental conditions.

The time course of the initial degradation of Biopol® bottles during the first 250 days on the sediment surface of an aquatic ecosystem at a water depth of 85 m is shown in Fig. 2. Assuming a zero order (constant rate vs. time) reaction, a life span of approximately ten years was calculated for this specific bottle type. The microbial attack of the plastic material was not homogeneous as judged macroscopically from the presence of pits and cavities on the surface of the shampoo bottles. A possible explanation is the heterogeneity of the sediment matrix as well as the small scale spatial patchiness of microbial activities.

Dependent on the water depth (and therefore on temperature, oxygen content, hydrostatic pressure, and other chemical and physical parameters), the degradation rates of PHA bottles decreased with increasing depths (Fig. 3). In contrast to the degradation in the surface sediments the pattern of microbial attack was homogeneously distributed over the bottle's surface.

In order to study the depth distribution of the PHA degradation potential in surface sediments and the near bottom lake water, pieces of PHA film were incubated in different sediment horizons and in the overlaying water column. All of the PHA films were degraded almost completely within the incubation period of 254 days. No difference was observed between the different sediment layers and the hypolimnetic water indicating the presence of active microbial populations capable of degrading BIOPOL® in both the highly reduced anoxic sediment ecosystem and the near bottom lake water.

SEM photographs of the eroded surfaces of the remaining pieces of Biopol® film are presented in Fig. 4. The films exposed to lake sediments showed a relatively smooth surface before incubation (Fig. 4a and 4c, respectively). Distinct cavities and pores due to microbial degradation processes are visible after the incubation period of 260 days (Fig. 4b and 4d, respectively).

Discussion

PHB homopolymer as well as PHA copolymers have been demonstrated as being biologically degraded either by hydrolytic or enzymatic reactions (Brandl et al. 1990; Delafield et al. 1965; Chowdhury 1963; Doi et al. 1990; Holland et al. 1987; McLellan & Halling 1988; Miller & Williams 1987; Nakayama et al. 1985). However, all of the studies published so far have been done in the laboratory under controlled conditions. Here we report on a field study in order to determine the degradation characteristics of Biopol® shampoo bottles and PHA films in a natural ecosystem (freshwater lake) under *in situ* conditions.

Assuming a zero order degradation reaction of the plastic material (Fig. 2), a life span of five to ten years can be expected for the specific bottle type used in this study when incubated in the water column and on the sediment surface. However, the degradation is a function of the surface area available for microbial attack. Therefore, the calculated half lives are maximal values, because the surface area increases with time due to the formation of cavities and pores.

Biopol® films were completely degraded within the incubation period of 254 days at *in situ* temperatures not exceeding 6 °C (Fig. 1). Recently, the complete degradation of poly(3-hydroxybutyrate-co-hydroxyvalerate) films within 60 days at temperatures of 37 °C and 58 °C under laboratory conditions has been demonstrated (Krupp & Jewell 1992).

The results of our field clearly demonstrate that in an aquatic ecosystem under *in situ* conditions (seasonal changes of the oxygen concentration from anoxic to oxic conditions, low temperatures), commodity plastic articles made from PHA, such as shampoo bottles or films, are degraded.

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