Pure Appl. Chem., Vol. 71, No. 11, pp. 2177–2188, 1999.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION
COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

STUDIES ON BIODEGRADABLE POLY(HEXANO-6-LACTONE) FIBERS. PART 2: ENVIRONMENTAL DEGRADATION

(Technical Report)

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Studies on biodegradable poly(hexano-6-lactone) fibers. Part 2: Environmental degradation (Technical Report)

Abstract: Poly(hexano-6-lactone) (PCL†) fibers were degraded under environmental conditions, including soil burial, seawater exposure, and activated sludge exposure. The extent of degradation was examined by weight loss, loss of mechanical properties, such a tensile strength and ultimate elongation decreases, and visual observations by scanning electron microscopy. The rate of degradation was found to depend on the draw ratio and crystallinity of the PCL fibers with surface erosion of amorphous regions more readily than crystalline regions. The life-time of highly drawn PCL fibers when exposed to soil burial and seawater was evaluated from the viewpoint of environmental applications. In terms of the degradation mechanism of PCL fiber breakdown, biodegradation seems to be the dominant reaction, that is a hydrolysis reaction catalyzed by enzymes secreted by microorganisms.

INTRODUCTION

Poly(hexano-6-lactone) (PCL†) is an aliphatic polyester which is susceptible to assimilation by microorganisms such as fungi and bacteria. PCL has been extensively studied for biodegradability since the work of Darby and Kaplan [1], who found that polyurethanes based on aliphatic polyester diols were more susceptible to fungal attack than those based on polyether diols. Potts *et al*. [2] molded PCL with a molecular weight of about 40 000 into tensile test bars and buried them in soil. At the end of 12 months, the bars were too weak for the measurement of strength properties and had lost 42% of their original weight. Fields *et al*. [3] analyzed the activity of *Pullularia pullulans* towards PCL of different molecular weights and found negligible degradation of molecules above a molecular weight of 15 000 by measuring the weight loss of cast films. Diamond *et al*. [4] found that PCL films were highly degraded in both the agar culture with *Aspergilli* and soil burial tests. Tokiwa *et al*. [5] reported that PCL with a molecular weight of 25 000 was completely degraded by *Penicillium* sp. 26-1 isolated from soil. They [6] also studied the biodegradation of a variety of polyesters with various enzymes and found that aliphatic polyesters such as PCL were degraded by lipases. Cook *et al*. [7–9] have shown that the amorphous regions of PCL films are degraded more readily than crystalline areas by scanning electron microscopy visualization. The reduced order within amorphous regions may facilitate enzyme diffusion to available linkages.

High-molecular-weight PCL has been melt-spun into fibers with high tenacity, and the relationship between the microstructure and properties of the PCL fibers with various draw ratios was discussed in detail in a previous paper [10]. It is well known that PCL is a truly biodegradable thermoplastic, whose fiber has never been used as a bioabsorbable suture due to its slow rate of hydrolysis *in vivo*. The use of PCL in environmental applications, on the other hand, is of considerable interest. Environmentally degradable man-made fibers for commodity or industrial uses, such as agricultural mulch sheets, fishing nets, and cover stock for disposable diapers, are expected to be degraded by enzymes secreted by microorganisms in soil, compost, activated sludge and water. There has been, however, little study on the environmental degradation of PCL fibers so far. In the present study, the environmental degradation of PCL fibers with various draw ratios in soil, activated sludge and seawater is reported, and the effect of the solid-state morphology of the fiber structure upon the rate of biodegradation is discussed.

†The name 'ϵ-caprolactone' is commonly used rather than the IUPAC nomenclature 'hexano-6-lactone'; hence the abbreviation PCL, based on the former, is used throughout this Technical Report.

EXPERIMENTAL

Materials

The PCL polymer is available from Union Carbide Corporation under the trade name TONE. TONE P-787 is a tough, extensible polymer with a number-average molecular weight (M_n) of about 80 000, and consequently it was used to prepare a high tenacity fiber. Tough and high tenacity PCL multifilaments (72d/24f) and monofilaments (740d) of TONE P-787 were prepared by melt-spinning at 210 °C with subsequent drawing. Furthermore, monofilaments with almost the same diameters (280 ± 5 μm) and different draw ratios (undrawn to nine times drawn) were prepared. The structure and properties of the monofilaments were described in detail in a previous paper [10].

In order to compare the rate of degradation of PCL fiber in soil with other materials, drawn multifilaments of almost the same diameter (17.0 ± 2.5 μm) of nylon 6 (70d/24f, 19.0 μm), poly(ethylene terephthalate) (75d/36f, 14.7 μm), poly(vinyl alcohol) (1200d/500f, 16.2 μm), rayon (75d/30f, 15.3 μm), and PCL (150d/72f, 16.1 μm) were prepared.

Soil burial tests

Soil burial was carried out in the garden (soil: coarse sandy loam) of Unitika Research and Development Center from July 5, 1991 to September 20, 1991; a 10 m length of each test specimen of fiber was wound on skein and buried at a depth of 10 cm from the ground surface. The test specimens were periodically removed from the soil, a sufficient length was unwound to perform five replicate tensile tests, and the specimen was then gently washed to remove attached soil and dust. After being dried in a vacuum oven, the extent of degradation was examined by weight loss, relative viscosity reduction, tensile strength decrease, and microscopic surface observation.

Activated sludge exposure tests

Test specimens of PCL multifilaments for activated sludge exposure were placed into a nylon mesh bag and immersed in fresh sewage sludge from the wastewater treatment plant of the Unitika Uji Plant, Uji, Kyoto, Japan. The test specimens were periodically removed from the activated sludge and gently washed with distilled water, followed by drying, to examine the tensile strength and ultimate elongation decreases.

Seawater exposure tests

Test specimens of PCL monofilaments for seawater exposure were placed into a nylon mesh bag and suspended at a point 1 m in depth under the seawater surface of Tokyo Bay, Kawasaki, Kanagawa, from October 21, 1991 to December 12, 1991, and of Osaka Bay, Misaki-cho, Osaka, from October 5, 1992 to December 17, 1992. The test specimens were periodically removed from the seawater and gently washed with distilled water, followed by drying, to examine the weight loss, tensile strength decrease, and microscopic surface observation.

On the other hand, undrawn PCL monofilaments were degraded in different aqueous media, including distilled water (25 °C, pH 7.0), phosphate buffer solution (36 °C, pH 8.68), and a beaker of seawater (25 °C) in order to examine the major cause of degradation in a marine environment.

Counts of bacteria adhering to undrawn PCL monofilament exposed to seawater were conducted by the most probable number (MPN) method as follows: 50 ml of sterilized seawater with 0.1% Tween 80 was added to a sterile homogenizer containing 500 mg of the PCL monofilament, and the mixture was homogenized to give a microbial suspension; the homogenized suspension was diluted with sterilized seawater by the 10-fold dilution method and a definite amount of each suspension was inoculated to a basal medium (α medium) which contained: Bacto-Casitane, 5 g; beef extract, 3 g; KNO_3, 0.5 g; KH_2PO_3, 0.1 g; seawater, 1000 mL; 4 ml of each α medium inoculated with the dilutant from the bacterial suspension was poured into a test tube containing 5 cm of a sterilized sample and was incubated at 25 °C for 2 weeks. The MPNs of total and PCL-degrading bacteria were determined by the numbers of dilution steps of positive test tubes.

Tensile and knot tests

Using a tensile testing machine, Autograph S-100 (Shimadzu Co.), tensile and knot properties of PCL fibers were measured in accordance with a standard method, JIS L-1013. A crosshead speed of 30 cm/min and a gauge length of 25 cm were used for drawn fibers, and a crosshead speed of 10 cm/min and a gauge length of 2 cm were used for undrawn fibers.

Surface observations

Before and after degradation tests, the surfaces of the PCL fibers were observed using field emission type scanning electron microscopy (SEM) (S-4000, Hitachi Ltd.) with 4 kV acceleration after Au/Pd coating with an ion coater.

Relative viscosity measurements

Relative viscosity was measured by an Ubbelohde viscometer at a mass fraction concentration of 1% in toluene at 25 ±0.5 °C in accordance with JIS K-6726.

Density measurements

Densities of PCL fibers with different draw ratios were measured by a density gradient column of NaCl aqueous solution at 20 ± 1 °C as described previously [10].

RESULTS AND DISCUSSION

Soil burial tests

Percentage decreases in tensile strength and ultimate elongation of nine times drawn PCL monofilament and three times drawn multifilament as a function of time in soil burial are illustrated in Figs. 1 and 2, respectively. It can be seen that the rate of degradation of the multifilament (3 denier per filament) is much faster than that of the monofilament (740d). This may probably be attributed to the greater surface-to-volume ratio of the multifilament. With regard to the half-degradation time for the fibers to lose 50% of their initial tensile strength when in contact with the soil, Fig. 1 indicates that this is about 1 month for the monofilament (Class 3, diameter: 280 ± 5 μm) and about 1 week for the multifilament. After 3 months for the monofilament and 2 weeks for the multifilament, the fibers became brittle and fragmented very easily, which made it impossible to measure their physical properties any longer.

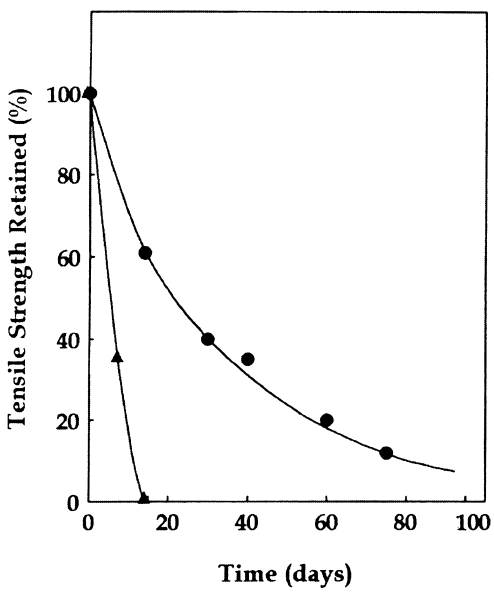

Fig. 1 Changes in tensile strength of PCL monofilament and multifilament during soil burial: ●, monofilament; ▲, multifilament.

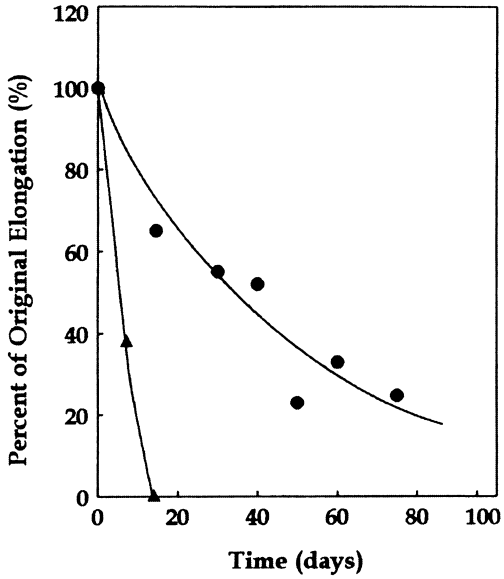

Fig. 2 Changes in ultimate elongation of PCL monofilament and multifilament during soil burial: ●, monofilament; ▲, multifilament.

One of the most useful means of measuring the extent of degradation is viscometry; important information such as molecular weight can be obtained. Figure 3 shows the change in the relative viscosity of the residual PCL monofilament during soil burial, indicating that the values did not undergo any significant change, even after 75 days of soil burial. Thus, in terms of the degradation mechanism of PCL fiber breakdown in soil, surface erosion with weight loss appears to be the dominant process.

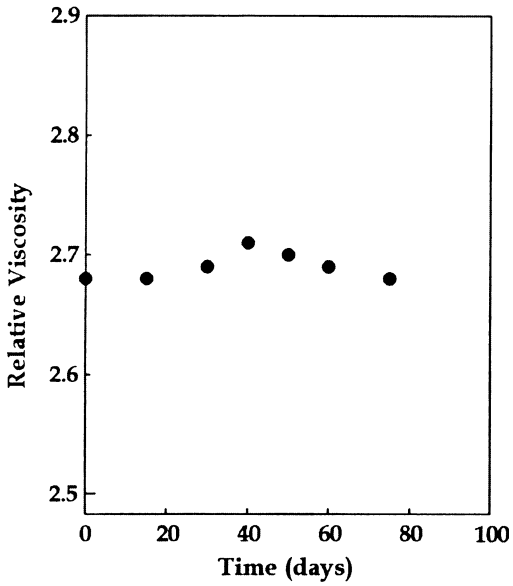

Fig. 3 Change in relative viscosity of PCL monofilament during soil burial.

SEM photographs of the PCL monofilaments before and after soil burial are shown in Figs. 4a–4c. Figure 4b shows clear degradation of the monofilament surface with significant discrete depression at the area around the traces of microbial colonies after 1 month of burial. The monofilament developed severely hollow surfaces with mycelial growth after 2 months of burial, as shown in Fig. 4c. The filamentous fungi are widely recognized as being a major cause of biodeterioration of natural polymers and their ability to degrade PCL has been reported [4,6,7]. The initial step of biodegradation is a random

scission of the in-chain ester linkage of the polymer by extracellular enzymes secreted by microorganisms, ultimately resulting in the formation of water-soluble products followed by their removal. Thus, the surface erosion mechanism was supported by the SEM observations and almost constant molecular weight of the residual sample during biodegradation.

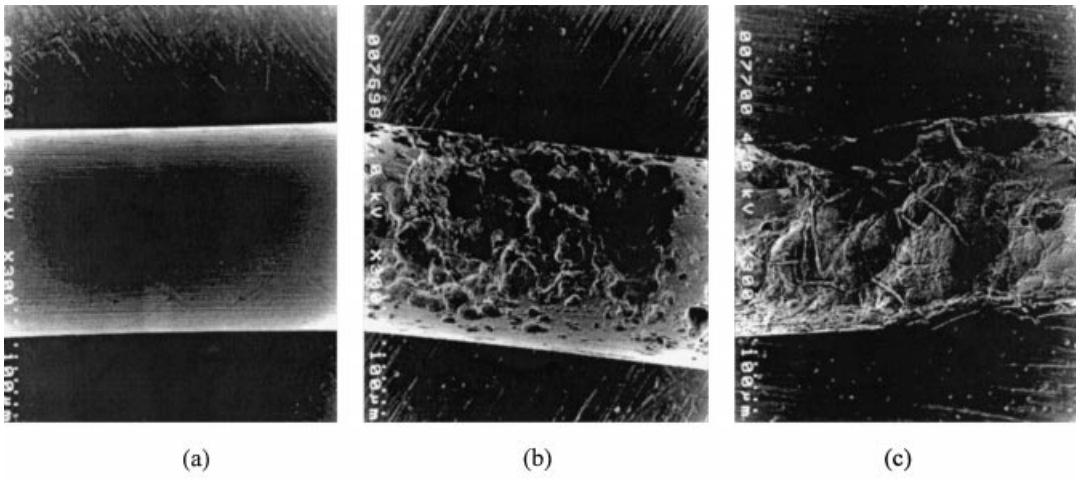

Fig. 4 SEM photographs of PCL monofilament before (a), after 1 month of soil burial (b), and after 2 months of soil burial (c).

In order to understand the effect of the solid-state morphology of the fiber on biodegradation, the soil burial tests were carried out for PCL monofilaments with different draw ratios, but with the same radius (280 ± 5 μm). We have plotted the rate of biodegradation against crystallinity and a linear relationship is observed as shown in Fig. 5. The initial rate of biodegradation of the undrawn fiber is ten times faster than that of the nine times drawn fiber, probably due to the lower crystallinity. This suggests that enzymes secreted by microorganisms attack preferentially the amorphous or less ordered region rather than the crystalline or more ordered region, because the enzymes are able to migrate more readily into the less ordered region than the more ordered region. The density of specimens increased during soil burial tests for a period of 9 months as shown in Fig. 6. This is probably attributed to the preferential degradation and removal of amorphous regions. However, the possibility of cold crystallization of macromolecular chains in connection with water absorption cannot be excluded [11].

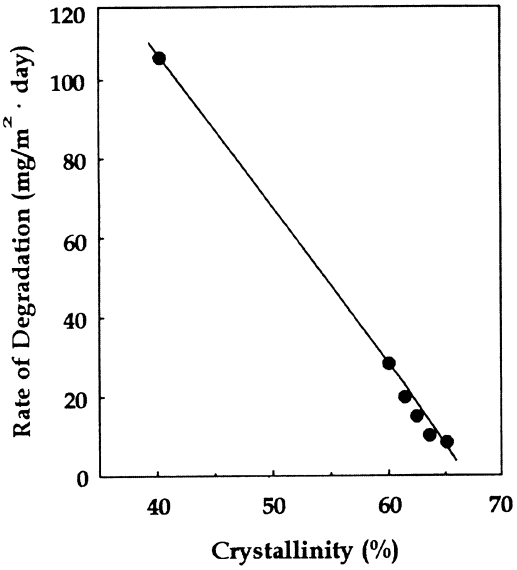

Fig. 5 Relationship between the rate of degradation in soil and the crystallinity of PCL monofilaments.

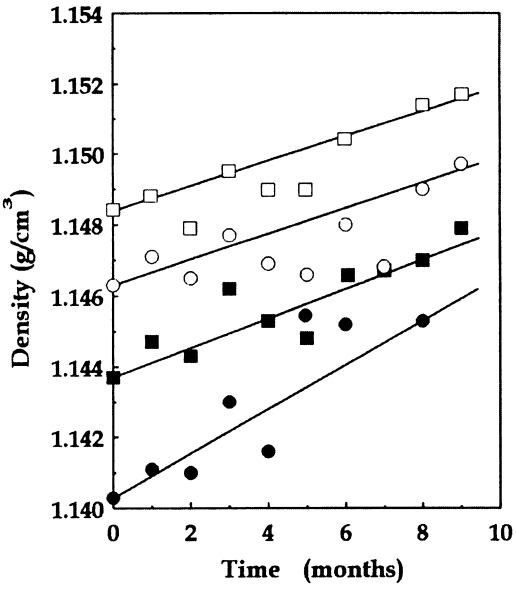

Fig. 6 Changes in density of PCL monofilaments with different draw ratios during soil burial: ●, undrawn; ■, 5 times drawn; ○, 8 times drawn; □, 9 times drawn.

Figure 7 shows the percentage decreases in tensile strength of various multifilaments with almost the same diameter (17 ± 2.5 μm) versus time of soil burial. The PCL fiber as well as the rayon lost almost 100% of the tensile strength within a week, while the fibers of nylon 6, poly(ethylene terephthalate), and poly(vinyl alcohol) retained 60–90% of initial tensile strength even after 50 days, suggesting that these fibers were resistant to microbial attack. The unique pattern of surface erosion of the PCL multifilament subjected to 2 weeks of soil burial is shown in Fig. 8, revealing a number of fine cracks perpendicular to the fiber axis. Chu *et al.* [12] observed the surface of γ-irradiated poly(glycolic acid) sutures exposed to hydrolytic degradation and reported the formation of fine cracks perpendicular to the fiber axis. Almost the same pattern of cracks was observed all over the surface for poly(L-lactide) fiber subjected to hydrolytic degradation at 100 °C [13]. With regard to the morphology of the fiber structure, the microfibrillar model with chain folds [14] and the interlocking shish-kebab structure [15], in which alternate crystalline and amorphous regions are arranged in the direction of the fibers, are well known. Therefore, it is believed that hydrolysis occurs initially in the amorphous regions sandwiched between two crystalline zones, as tie-chain segments, free chain ends, and chain folds in these regions degrade into water-soluble fragments.

Activated sludge exposure tests

Percentage decreases in tensile strength and ultimate elongation of the same samples as those for the soil burial test as a function of time of activated sludge exposure are shown in Figs 9 and 10, respectively. When compared with the soil burial test (Figs. 1 and 2), the rate of degradation in activated sludge is much slower than that in soil burial, although the patterns of degradation are similar. The half-degradation time of the monofilament is expected to be 120–150 days.

Seawater exposure tests

Percentage decreases in tensile strength and percentage weight losses of PCL monofilaments with different draw ratios (undrawn, five times drawn, nine times drawn) during seawater exposure at Osaka Bay are shown in Fig. 11. They give a quantitative indication of the differences in the degradation rates of the fibers with different draw ratios. The rate of tensile strength decrease and weight loss decreased with an increase in draw ratio in the same manner as in the soil burial test. A dramatic decrease (half-degradation time, 3 days) in tensile strength was observed for the undrawn fiber, whereas the nine times drawn fiber showed a gradual decrease (half-degradation time, 30 days) in tensile strength. The

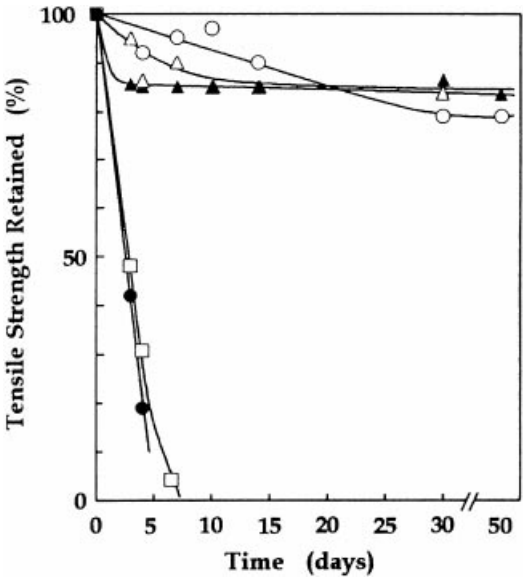

Fig. 7 Changes in tensile strength of various kinds of multifilaments with almost the same denier per filament during soil burial; ●, rayon; □, PCL; ○, poly(vinyl alcohol); △, nylon 6; ▲, poly(ethylene terephthalate).

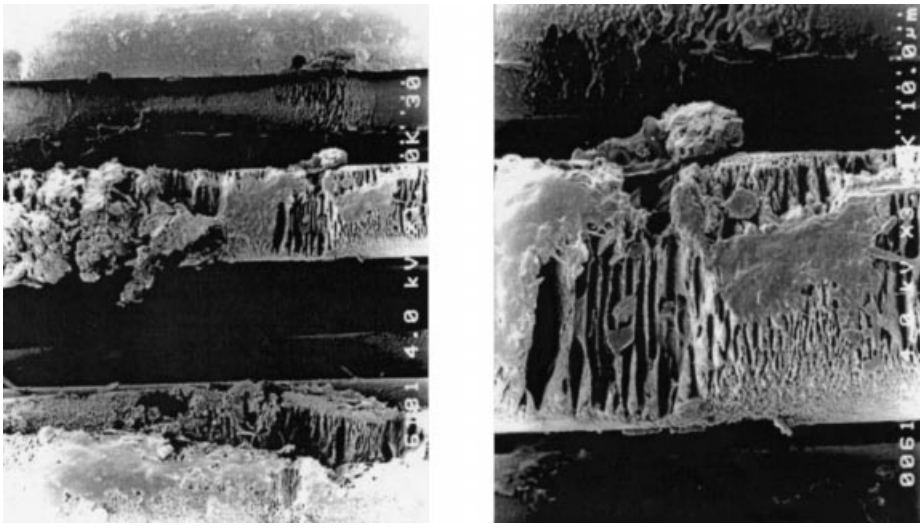

Fig. 8 SEM photographs of PCL multifilament after 2 weeks of soil burial.

appearances of undrawn PCL samples before and after seawater exposure are shown in Fig. 12, and are similar to those of soil burial, revealing spherical holes probably resulting from localized enzymatic action with colonization of degrading bacteria. All PCL monofilaments rapidly lost their mechanical properties before significant weight losses were observed, as can be seen in Fig. 11. This might be caused by the fact that the tensile strength is a more sensitive measure of the extent of degradation than is the weight loss, because failure occurs at cracks or stress concentration points in the samples.

Table 1 shows the results of degradation of undrawn PCL monofilaments in various aqueous media. Both distilled water and phosphate buffer solution showed only slight degradation when compared with that under seawater conditions, suggesting that chemical (non-enzymatic) hydrolysis is not the primary mechanism in hydrolytic degradation. On the other hand, the sample was severely degraded when exposed to seawater, especially fresh and biologically active seawater. Thus biologically degradation, such as enzymatic hydrolysis by microorganisms, is assumed to be the primary mechanism.

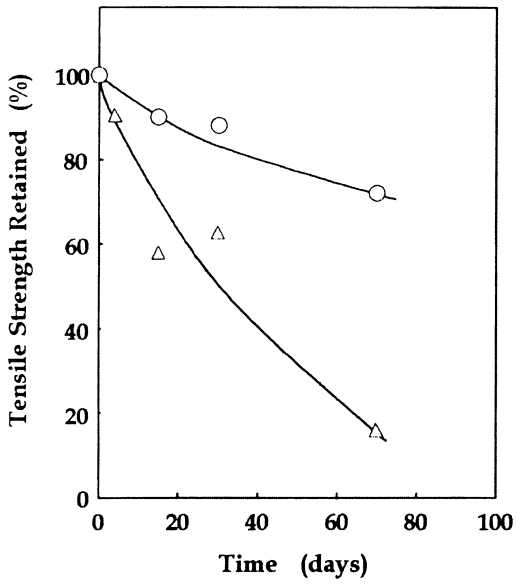

Fig. 9 Changes in tensile strength of PCL monofilament and multifilament during activated sludge exposure; ○, monofilament; △, multifilament.

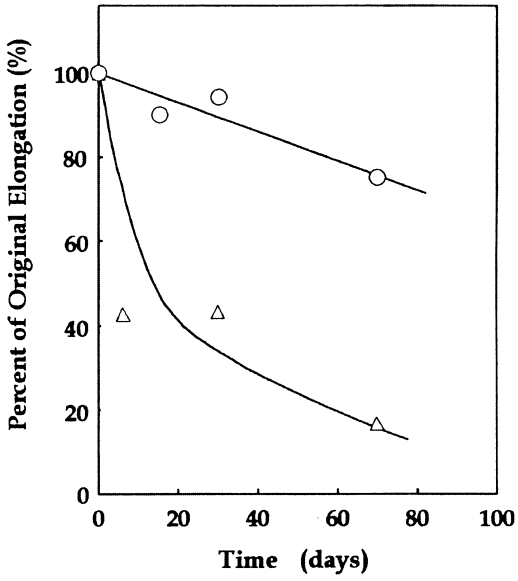

Fig. 10 Changes in ultimate elongation of PCL monofilament and multifilament during activated sludge exposure; ○, monofilament; △, multifilament.

Table 2 shows the MPN of total and PCL-degrading bacteria, attached to the undrawn PCL monofilament (525 mg) subjected to 45 days of seawater exposure. A PCL-degrading bacterium isolated from seawater was identified as *Pseudomonas* species.

Figure 13 shows the results of the sea exposure test at Tokyo Bay. The differences in the rate of degradation between different fiber diameters can be clearly seen, i.e. the rate of degradation of the finer fibers is much faster because of the greater surface area, as in the case of soil burial tests. The profiles of the tensile strength decrease and weight loss for Osaka Bay and Tokyo Bay were quite similar.

In this report, the rate of degradation in the marine environment was faster than that in soil. However, this generally depends upon the geographic location, environmental conditions, and bacterial species and populations.

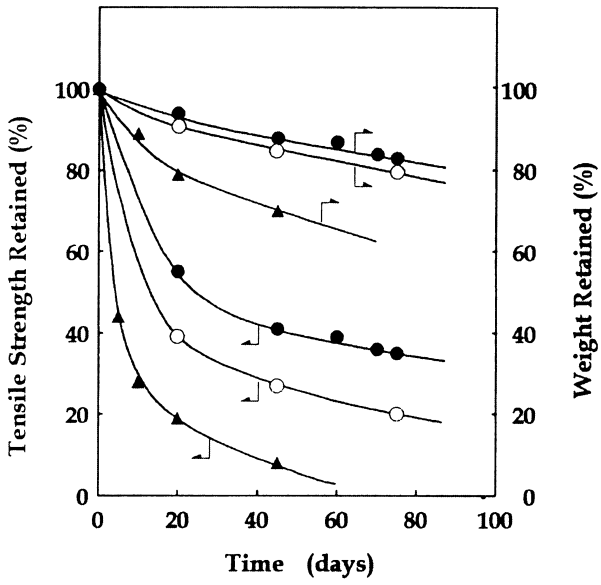

Fig. 11 Changes in tensile strength and weight of PCL monofilaments with different draw ratios during seawater exposure at Osaka Bay; ▲, undrawn; ○, 5 times drawn; ●, 9 times drawn.

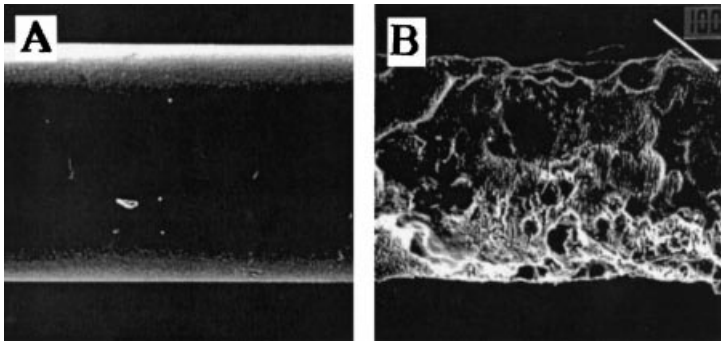

Fig. 12 SEM photographs of undrawn PCL monofilament before (A) and after 46 days of seawater exposure (B).

Table 1 Degradation of undrawn PCL monofilaments in various aqueous media

Medium (condition)	Time (days)	Tensile strength (g)	Ultimate elongation (%)	Remarks
Original	0	550 ± 50	1061	
Pure water (25 °C, pH 7.0)	72	495 ± 55	1188 ± 80	Clear
Phosphate buffer solution water (36 °C, pH 8.7)	54	490 ± 45	1132 ± 45	Clear
Seawater in flask (25 °C)	76	330 ± 40	881 ± 5	Hazy & stinking
Fresh seawater (15 °C)	25	90 ± 25	582 ± 70	

Table 2 Most probable numbers (MPNs) of total and PCL-degrading bacteria attached to the undrawn PCL monofilament subjected to 45 days of seawater exposure

Bacteria	MPN (cells/g)
Total	9.2×10^9
PCL-degrading bacteria	2.4×10^5

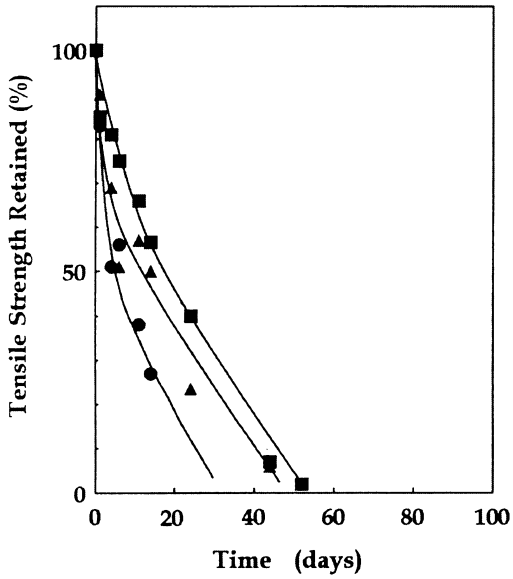

Fig. 13 Changes in tensile strength of PCL monofilaments with different deniers during seawater exposure at Tokyo Bay: ●, 223 denier; ▲, 670 denier; ■, 1129 denier.

CONCLUSION

There are microorganisms in soil, activated sludge, and seawater that have the ability to degrade PCL fibers. It would appear from our results that the degradation profile of the PCL fiber depends on both the environmental conditions and the fine structure of the fiber. The half-degradation times of drawn PCl monofilaments ($280 \pm 5\,\mu m$) are 30–40, 120–150 and 15–30 days for soil burial, activated sludge exposure, and seawater exposure, respectively. The microbial degradability was decreased with increasing crystallinity by drawing, and with increasing diameter of the fiber.

Surface erosion with weight loss by extracellular degradation enzymes secreted by microorganisms appears to be the primary mechanism in environmental degradation of PCL fibers. The delay in the molecular weight loss in comparison with weight loss is evidence of surface degradation, which was supported by visual observations by scanning electron microscopy. The microbial degradation proceeded in two ways. One was spherical depression on the fiber surface, which results from localized enzymatic action with colonization of the degrading microorganisms. The other was preferential enzymatic degradation of the amorphous regions, leaving a number of cracks perpendicular to the fiber axis. The microfibrillar and shish-kebab models of fiber structure were employed to provide the basis for the proposed degradation mechanism of PCL fibers.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Professor Akira Kawai and Associate Professor Mitsuru Eguchi of Kinki University for their advice and assistance in field tests in the marine environment.

APPENDIX

List of abbreviations

MPN most probable number

PCL poly(hexano-6-lactone)

SEM scanning electron microscopy

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