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Biodegradation of poly (ε-caprolactone) monofilament fibers in deep seawater at near 0 ℃

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Abstract

An application of environmentally degradable plastics for fishing nets may help solve the ghost fishing problem. In this study, biodegradation of aliphatic polyester, poly(ε -caprolac tone) (PCL) was studied in deep seawater under a low temperature of 0.6 °C during the period of 8 months at atmospheric surface pressure. Processes of biodegradation were analyzed by monitoring the time-dependent changes in mechanical strength and scanning electron micrographs (SEM) of the surface of PCL monofilaments. The strength of 110 D fibers decreased to about 80 % of initial value after one month of soaking, about 60 % after three months and about 35 % after six months. After eight months of soaking, the filament did not keep its original shape and the strength reached zero. Thus it could not be subjected for the strength measurement any further. From SEM micrographs of PCL monofilament fibers soaked in deep seawater for 3 and 8 months, pinholes were observed on the surface of treated fibers. The number of these pinholes increased with the soaking period. This phenomenon strongly suggested that the degradation of PCL in deep seawater is caused at least partly by microbial degradation. From these results, the application of biodegradable plastics such as PCL for fishing gears is suggested to be effective in reducing ghost fishing problem caused by non-biodegradable fishing nets.

Key Words: ghost fishing, biodegradable polymer, poly (ε-caprolactone), deep seawater, biodegradation

Every year, several hundred thousand tons of discarded plastic products contaminate the marine environment via various waterways, causing marine pollution, and harming numerous marine animals potentially resulting in their death (Laist 1987). Some plastic fishing gear is also left at the sea floor as a result of unintentional loss during ordinary fishing operations. It has been reported that some lost fishing gear could maintain their fishing ability for several years under unattended, such as ghost fishing (Kanehiro *et al.* 1995). For example, approximately 5000 gillnets were estimated to be lost annually in Newfoundland during cod fishing in 1970s (Smolowiz 1978). Canadian fishery consultants also estimated that around 8000 gillnets were lost annually in Canadian Atlantic waters (CFCL. 1994). Vienneau *et al.* (1984) dem-

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onstrated that snow crab pots were still capable of catching crabs for at least one year after abandonment by fisherman in the St. Lawerence River (Vienneau *et al.* 1984).

If fishing gear is made of biodegradable polymers which can be decomposed by microorganisms, instead of non-biodegradable plastics, ghost fishing is expected to be much reduced in marine environment. Therefore, there has been a growing latent demand for an application of biodegradable plastics to fishing gear. Some aliphatic polyesters attract much attention due to their biodegradability in soil (Doi *et al.* 1992, Kasuya *et al.* 1998). The biodegradation behavior and mechanism in surface seawater has also been reported for some aliphatic polyesters such as poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate), poly(ε-caprolactone) and poly(L-lactic acid) (Doi *et al.* 1992, Kasuya *et al.* 1998, Mukai et al. 1993, Rutkowsk et al. 1999, Tsuji *et al.* 2002, Ebisui et al. 2003). While, these biodegradable plastics have been developed for agricultural applications and wrapping materials, they have not been examined in fisheries science. According to the definition for biodegradability made by the Biodegradable Plastics Society (BPS), implying the conditions of land and composting at 20 - 58 ℃, many researches have employed this range of temperature for biodegradability examination (Doi *et al.* 1992, Kasuya *et al.* 1998, Mukai et al. 1993, Rutkowsk *et al.* 1999, Tsuji *et al.* 2002).

Abyssal environmental conditions of deep sea have not been clarified sufficiently, particularly in regards to biopolymer degradation. Since deep-sea conditions such as high pressure, saturated dissolved oxygen levels and low temperature are different from those on land and composting, it is expected that microorganisms will be less active in biopolymer decomposition. When fishing gear, such as crustacean pots, are lost during fishing, ghost fishing would occur in the deep sea rather than at the surface. Therefore, natural degradation needs to be studied under deep-sea conditions in order to minimize ghost fishing.

Among conditions mentioned above, water temperature seems to influence remarkably on the biodegradation by the microorganisms since enzymatic activity varies depending on ambient temperature. In this paper, we focused on degradability of poly (ε-caprolactone) (PCL) in actual deep seawater at a low temperature of 0.6 ℃. PCL is a well-known biodegradable aliphatic polyester that is synthesized from ε-caprolactone by ring-opening polymerization. This polymer has been known to be biodegraded by microbiological action not only on land but also in surface sea, river and lake waters.

Biodegradation tests of PCL samples in deep seawater started on April 2003 for a period of up to 8 months. Deep seawater pumped at 320 m depth from 2600 m offshore in Toyama Bay was used for the biodegradation test. PCL monofilament fibers with different denier (D: designation of linear density of fibers (JIS L1073)) of 110 D, 300 D, and 500 D were purchased from Chukou Chemical Industries, Ltd. Six monofilament fibers of 40 cm of each denier were bundled together with nylon strings and put in the polyester nets. Four sets of these bundles were soaked into deep seawater under complete darkness in the FRP tank (10 tons) at the Toyama Prefectural Fisheries Research Institute. This tank was always filled with running fresh deep seawater at a flow rate of 3.5 tons/hr. and controlled at 0.6 ℃. One set of the bundles was taken out from the tank after one, three, six and eight months, respectively, washed with water and air dried to be subjected

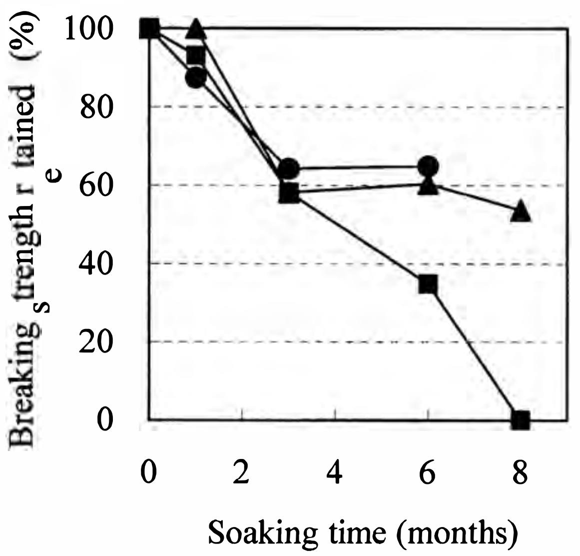

Fig. 1. Time-dependent changes in breaking strength of PCL monofilament fibers in deep sea water at 0.6 ℃. ■: 110D, ●: 300D, ▲: 500D

to the measurement of breaking strength. The measurement was performed with an Auto graph (Shimazu;AG-1) under the conditions of 25 ℃ and 60 % humidity, initial material interval of 50 mm and crosshead speed of 100 mm/min. The surface morphology of the fibers was examined under a scanning electron microscope (SEM, Hitachi S-2000) with secondary electrons at acceleration voltage of 3 kV at room temperature.

The breaking strength of intact PCL monofilament fibers of 110 D, 300 D and 500 D were 0.34 kg, 0.96 kg and 1.38 kg, respectively. The relative retained breaking strengths of PCL fibers soaked in deep seawater are plotted against soaking time (Fig. 1). The strength of 110 D fibers decreased to about 80 % of the initial value after one month soaking. Then it became about 60 % in three months and about 35 % in six months. Eight months later, the filament did not keep its original shape and thus could not be subjected for the strength measurement. Fibers of 300 D and 500 D showed similar behaviors for the reduction of their strengths for the first 3 months. The strength decreased gradually to become 60 % within 3 months. When these fibers were soaked for 6 months, the strengths remained at the 60 % level like those of 3 months soaking. The difference in degrading behaviors according to the fiber denier showed that thinner fibers were degraded faster.

Fig. 2 shows the SEM micrographs of the 300 D monofilament fibers soaked in deep seawater for 3 and 8 months, compared with the intact fibers (Fig. 2, A and B). On the surface of treated fibers, pinholes were observed. The number of these pinholes increased with soaking period. If PCL monofilament fibers are degraded by chemical hydrolysis with seawater, they are presumed to become thinner homogeneously. However, as shown in Fig. 2, the fibers were degraded with heterogeneous erosion accompanied by formation of pinholes. This phenomenon suggests that certain microorganisms grow their colonies on the surface of fibers and eroded parts of the fiber surface contacting directly with the microorganisms. Although microorganisms were not detected on the fiber surface by the present observations by a scanning electron microscopy, it can be considered that only microorganisms adhered to the filament fiber can grow their colonies resulting in pinholes (Tabata et al. 2004). And, thus, the decrease in breaking strength can be considered to be caused at least partly by microbial degradation. This is in good agreement with the observed fact that thinner fibers with greater surface areas reduced their breaking strength faster (Fig. 1).

From these results, it is concluded that PCL monofilament fibers can be degraded under deep-sea conditions by possible microbial attack at atmospheric surface pressure. The application of PCL for fishing gears seems to be effective for

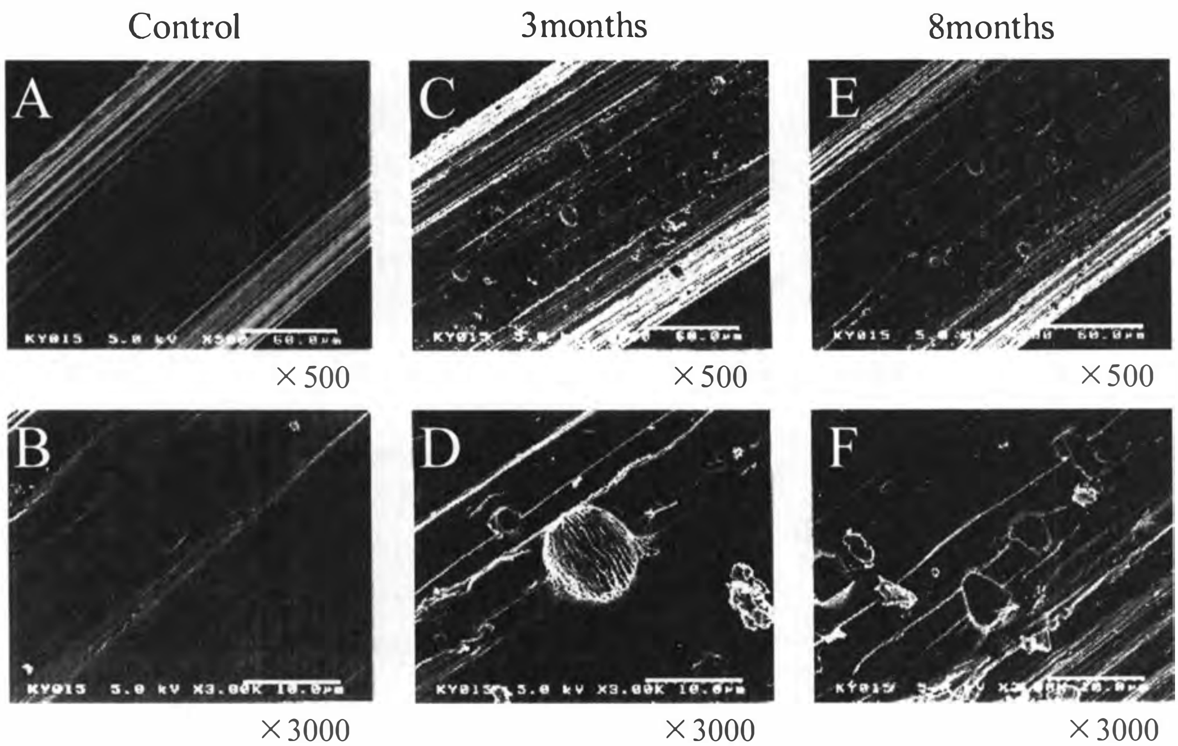

Fig. 2. Scanning electron micrographs of PCL monofilament fibers before (A and B) and after (C, D, E, F) soaking in deep sea water at 0.6 °C. A and B: before soaking, C and D: soaking for 3 months, E and F: soaking for 6 months

reducing the ghost fishing problem caused by non-biodegradable fishing nets.

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深層水中におけるポリカプロラクトン繊維の生分解

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要　旨

海洋に流出した漁網等によるゴーストフィッシング問題の解決の一つとして生分解性漁網の利用が検討されている．海水中における生分解性プラスチックの分解性に関する研究は少なく,特に深海域における分解性についてはほとんど知見がない．本研究では，富山県水産試験場の深層水汲み上げ施設の飼育水槽（流水式：常圧，平均水温 0.6 ℃）中で，生分解性プラスチックのポリカプロラクトン（PCL）モノフィラメントの浸漬試験を行い，深層水中における生分解性の評価を行った．0.6 ℃の深層水中に浸漬した PCL (110 デニール)の強度は浸漬時間とともに大きく低下していき（1ヶ月で約 20 %，6ヶ月で約 65 %低下），8ヶ月後には強度はほぼ 0 にまで低下していた．電子顕微鏡観察結果より，浸漬時間とともに繊維表面に小さな円形の穴が多数生じているのが認められた．繊維表面上に見られる円形の穴は浸漬水中に存在する微生物（プラスチック分解菌）による分解の進行にともなって起こったものと推測された．これらの結果から，生分解性プラスチックが低温の海洋深層水中で十分に分解することが確認され，ゴーストフィッシング軽減につながることが示唆された．

キーワード： ゴーストフィッシング，生分解性プラスティック，ポリカプロラクトン，深層水，微生物分解