<Original Paper>

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Enzymatic Degradation of Poly(Hexano-6-lactone) Fibers by
Copoly(Methylvinylether/Maleic anhydride)-Modified
Lipoprotein Lipase

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Abstract

Poly(hexano-6-lactone)(PCL) fibers were enzymatic degraded by lipoprotein lipase(LPL) modified with copoly(methylvinylether/maleic anhydride) (MAMEC) *in vitro*. The degradation of PCL fibers by MAMEC-modified LPL (MAMEC-LPL) was assessed by the weight loss and ultimate tensile strength loss. The experimental results were compared with those obtained with free LPL. The degradation kinetics on the weight loss of PCL fibers suggested that the degradation of PCL fibers gradually proceeded from the surface of fibers into their core. The weight loss of PCL fibers in the course of MAMEC-LPL digestion took place almost in parallel with the strength loss of PCL fibers, while the strength loss took place at a higher rate than the weight loss of PCL fibers in the course of free LPL digestion. The degradation of PCL fibers was found to depend on the draw ratio and crystallinity of PCL fibers.

Key words : Poly(hexano-6-lactone) fiber/Enzymatic Degradation/MAMEC-modified LPL/Mechanical Properties/

1. Introduction

Environmental pollutions brought about by plastic wastes have become a global problem. One of the solutions to the problem on plastic wastes is an application of biodegradable thermoplastics which degrade in soil, sea, lake, or river water, activated sludge, and compost after their service life has been over. It is interest to consider the use of biodegradable plastics from the view point of environmental applications that environmen-

tally degradable man-made fibers¹⁾ 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.

Poly(hexano-6-lactone)(PCL) is an aliphatic polyester that is relatively stable synthetic polymer under usual conditions and is biodegradable under microbial attack²⁻⁴⁾. poly(hexano-6-lactone) is the IUPAC nomenclature of the commonly used name, poly(ϵ -caprolactone). Hence the abbreviation PCL, based on the later, is used throughout this paper. PCL is a partially crystalline polymer that has a moderately low melting point of 60°C. PCL is susceptible to being assimilated by a microorganisms such as fungi and bacteria. Environmental degradation of PCL has been extensively studied for the biodegradable plastics⁵⁻⁹⁾. It was also studied about the biodegradation of a variety of polyesters with various enzymes, and it was found that aliphatic

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polyesters such as PCL were degraded by lipases. Furthermore, it was shown that the amorphous regions of PCL films are degraded more readily than crystalline regions by scanning electron microscopy (SEM) visualization as well as thermal analysis¹⁰⁻¹².

In a previous paper, the environmental degradation of PCL fibers with various draw ratios in soil, activated sludge, and sea water was reported¹³. The extent of degradation was examined by weight loss, loss of mechanical properties, and visual observations by SEM. 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 amorphous part of the film-blown PCL samples is degraded prior to the crystalline part in a biotic environment^{11,12}. Enzymatic degradation of the PCL fibers with various draw ratios *in vitro* by lipase was also studied to compare the behavior of the environmental degradation^{14,15}.

Since the biggest problem of free enzymes is the lack of stability, modification of enzyme molecules with a proper water-soluble polymer is considered very useful to stabilize the enzyme and preserve its activity retaining its solubility in water^{16,17}. In the previous paper, modification of LPL with polyethyleneglycol (PEG) or MAMEC was carried out based on covalent bonding. It was pointed out that thermal and storage stabilities of PEG-LPL and MAMEC-LPL were extremely higher than that of free LPL in spite of their lower relative activity [RA] than that of free LPL because of the deactivation by chemical modifications¹⁸.

In the present study, PCL fibers were degraded by LPL modified with MAMEC *in vitro*. The degradation of PCL fibers by MAMEC-modified LPL (MAMEC-LPL) was assessed by the weight loss, mechanical properties loss such as tensile strength and ultimate elongation decrease. The experimental results were compared with those obtained with free LPL. PCL fibers were also degraded by PEG-modified LPL (PEG-LPL)¹⁹ or copoly(L-glutamic acid/L-alanine)(EA)-modified LPL (EA-LPL)²⁰.

2. Experimental

2.1 Materials

The PCL monofilaments were prepared by melt-spinning at 210°C. The PCL monofilaments of TONE P-787 (The trade name of the PCL polymer by Union

Table 1 Physical properties of PCL fibers¹⁹

Draw ratio	Density (g/cm ³)	T _m (°C)	Degree of orientation	Crystallinity index (%)
DR=1 (undrawn)	1.1403	59	0.3368	40.0
DR=7 (drawn)	1.1446	62	0.9767	65.0

Carbide Co., Mn of about 80,000) were manufactured by Unitika Ltd., and kindly supplied for the present study. Tough and high tenacity PCL monofilaments with almost same diameters (280 ± 5 μm) were prepared. In this study, undrawn PCL and 7 times drawn PCL (DR=7) were used. The structure and properties of the PCL monofilaments were listed in Table 1 by the citation of the previous report²¹.

2.2 Preparation of MAMEC-modified LPL

In this study, lipoprotein lipase (LPL) (Amano Enzyme Co., Ltd.; Lipase-PS) from *Pseudomonas fluorescens* was selected as a hydrolytic enzyme. The LPL consists of two peptide chains linked by a disulfide bridge with a molecular weight of 33000²². Lipases (triacylglycerol acylhydrolase, EC 3.1.1.3) are widely found in animals, plants, and microorganisms. In particular, microorganisms are diversified in their enzymatic properties and substrate specificities²¹. Among them, Lipase-PS (abbreviates as LPL in this study) was found to have high specificities toward PCL hydrolysis^{15,18}.

As described above, enzymes undergo denaturation and, hence, deactivation by chemical modifications with water-soluble polymer carriers. Therefore, when an enzyme is chemically modified by MAMEC, one should carefully select the reaction conditions to minimize enzyme deactivation. MAMEC is a commercially available water-soluble polymer carrier, GANTREZ AN119 (GAF Chemical Co.), whose molecular weight is 872,000. Fig. 1 illustrates the scheme of chemical modification. The following is a typical modification procedure: 500 mg of MAMEC was solved in 15 ml of 0.1M

Fig. 1 Scheme of the modification reaction of LPL by copoly(methylvinyl ether/maleic anhydride: MAMEC)

phosphate buffer (pH 5.9, 20°C). 300 mg of LPL was added to the MAMEC solution under stirring, and the reaction mixture was stirred at 20°C for 24 h under stirring, and the solution was purified by repeated ultrafiltration with an Amicon PM-30 membrane. The extent of MAMEC modification was evaluated by determining the amount of free amino groups of LPL molecules according to the trinitrobenzene sulfonate method²³. The enzyme concentration was determined by the conventional biuret method²⁴. In this study, MAMEC-LPL sample was used whose degree of modification was about 39.5 wt% of LPL by MAMEC.

2.3 Assay of MAMEC-LPL and free LPL.

The hydrolytic activity of MAMEC-LPL and free LPL was determined by using 0.01M p-nitrophenyl laurate (pNPL) in 0.1M PBS at pH 7.0. After the reaction mixture was incubated under stirring for an appropriate time interval at 25.0°C, it was incubated by raising the temperature to 100°C for 5 min. The amount of p-nitrophenol produced was determining by measuring the absorbance of the solution at 400nm with Hitachi 101 spectrophotometer. The absorbance was plotted against LPL weight in the Reaction mixture, and the initial slope of the curve was used to evaluate the activity. In this study, the relative activity [RA, %] was used to evaluate the activity of MAMEC-LPL, which was defined as the ratio of the activity of MAMEC-LPL to that of the free LPL.

2.4 Degradation of PCL Fibers *in vitro*

The MAMEC-LPL as well as free LPL was dissolved in 0.1M PBS to yield solutions of known enzyme concentrations. The PCL fibers were placed in excess of the enzyme solution kept at pH 7.0 and 25.0°C, and then removed from the solution at appropriate time intervals. After vacuum drying at 40°C to constant weight, the remaining PCL fibers were weighed. The tensile strength of these fibers was measured for eight to ten samples of each fiber. The straight-pull tensile strength was determined with a Tensilon UTM- II -20 (Toyo-Boldwin Co.) at an elongation rate of 40% per min.

3. Results and discussion

3.1 Stability of LPL activity

It was shown that the enzymatic activity of pNPL hydrolysis of the MAMEC-LPL was lower than that of

Fig. 2 Effect of the storage time in 0.1M PBS (pH 7.0 and 25.0°C) on residual activity ZA of p-nitrophenyl laurate (pNPL) hydrolysis at pH 7.0 and 25.0°C: (1) (●) free LPL and (2) (○) MAMEC-LPL

the free LPL; RA=67%. This result may be caused by the lower change of an enzyme-substrate interaction, as well as the structural deformation of the MAMEC-LPL molecules through a covalent fixation process. The similar behaviors have been observed with PEG LPL¹⁸, though the experimental values of the enzymatic activity of pNPL hydrolysis were slightly different each other^{18, 20}.

To examine enzymatic stability in the continuous reaction system in aqueous solution, effect of the storage in 0.1M PBS (pH 7.0 and 25.0°C) were studied for MAMEC-LPL (39.5 wt% of LPL) and free LPL. The residual stability ZA at pNPL hydrolysis is given in Fig. 2. It is apparent that the LPL modified by covalent bonding with MAMEC is much more stable than the free LPL. Aqueous solutions of MAMEC-LPL could be stored at 25.0°C at least for 4 days without a significant loss of activity, whereas the free LPL lost more than 12% of its initial activity under the same conditions. On the other hand, it was reported that the thermal and storage stabilities of MAMEC-LPL were slightly higher than those of PEG-LPL in the same experimental condition¹⁸. It may be considered that the hydrophilic property of the methylvinylether group in MAMEC copolymer contribute to the retention of the enzymatic stability.

3.2 Degradation of Undrawn PCL Fibers *in vitro*

For the first time, the weight decrease of the undrawn PCL fibers subjected to degradation with free LPL as well as MAMEC-LPL was observed at pH 7.0

and 25°C in 0.1M PBS. Fig. 3 and 4 illustrate the dry weight ratio W_t/W_0 of the PCL fiber samples as a function of the degradation time in various initial enzyme concentration. It is shown that the rate of degradation depends on the enzyme concentration, respectively.

It is likely that the enzymatic degradation of the PCL fiber takes place from its surface in spite of the presence of water inside the fiber, since the enzyme molecule may be generally difficult to diffuse into the fiber interior because of the large size of the enzyme molecule and the rather low water content of the swollen fiber. The molecular weight of LPL is around 32,000 and the water content of the PCL fiber is less than 10%. If the enzymatic degradation takes place

from the fiber surface, the rate of weight decrease should be proportional to the total surface area of the fibers. This assumption leads to the following equation with the rate constant k as derived in the previous paper^{25, 26)}:

$$(W_t/W_0)^{1/2} = 1 - kt/r_0 d_0 \quad (1)$$

where W_0 and W_t are the weight of the fiber before and after degradation for time t , respectively, and r_0 ($=0.280$ mm) and d_0 ($=1.14$)⁹⁾ are the radius and the density of the starting fiber, respectively. Fig. 5 shows the plot of $(W_t/W_0)^{1/2}$ against t recalculated from the data given in Fig. 3. A linear relationship is obtained, at least, in the initial stage of the degradation. This linearity of the plot supports the assumption that the degradation of the undrawn PCL fibers take place from the fiber surface into the core. This degradation mode is quite different from that of the poly(glycolic acid) fiber which undergoes degradation almost homogeneously throughout the cross-section of the fiber from the beginning of degradation.

On the other hand, Fig. 6 shows the relation between $(W_t/W_0)^{1/2}$ and t recalculated from the data given in Fig. 4. A linear relation was obtained in the whole stage of experimental region. This complete linearity of the plot suggests that degradation of PCL fibers takes place almost only the surface region. This experimental result may be explained in terms of steric hindrance brought about by fixation of MAMEC chains. The rate constants of the degradation for the PCL fibers obtained from the initial slopes of the plots in Fig. 5 and 6, respectively, are shown as a function of the enzyme concentration $[E]$ in Fig. 7. It is shown that the k value for the undrawn PCL fibers depends on the enzyme concentration. As can be seen in Fig. 7, the data almost fit a straight line. Although this degradation proceeds heterogeneously, it obeys first-order kinetics similar to the usual homogeneous enzymatic reaction.

The surface of the PCL fibers were already observed by using a scanning electron micrographs (SEM) previously¹⁵⁾. Apparently, the fiber diameter decreased upon degradation, indicating that the enzymatic action *in vitro* proceeded from the surface of the PCL fibers.

3.3 Tensile Strength of Degraded PCL Fibers

In Fig. 8 and 9, the decrease in the tensile strength

Fig. 3 Dry weight ratio W_t/W_0 of the undrawn PCL fiber as a function of free LPL degradation time(h) at 25.0°C and pH 7.0 in 0.1M PBS: (1) $[E]=0.10$ wt%, (2) $[E]=0.15$ wt%, (3) $[E]=0.20$ wt%, and (4) $[E]=0.25$ wt%.

Fig. 4 Dry weight ratio W_t/W_0 of the undrawn PCL fiber as a function of MAMEC-LPL degradation time(h) at 25.0°C and pH 7.0 in 0.1M PBS: (1) $[E]=0.06$ wt%, (2) $[E]=0.12$ wt%, (3) $[E]=0.18$ wt%, and (4) $[E]=0.24$ wt%.

Fig. 5 $(W_r/W_0)^{1/2}$ of the undrawn PCL fiber as a function of free LPL degradation time (h) at 25.0°C and pH 7.0 in 0.1M PBS: (1) $[E]=0.10$ wt%, (2) $[E]=0.15$ wt%, (3) $[E]=0.20$ wt%, and (4) $[E]=0.25$ wt%.

Fig. 7 The rate constant, k , for the enzymatic degradation of the undrawn PCL fiber as a function of the concentration of LPL at 25.0°C and pH 7.0 in 0.1M PBS: (1) (●) free LPL and (2) (○) MAMEC-LPL.

Fig. 6 $(W_r/W_0)^{1/2}$ of the undrawn PCL fiber as a function of MAMEC-LPL degradation time (h) at 25.0°C and pH 7.0 in 0.1M PBS: (1) $[E]=0.06$ wt%, (2) $[E]=0.12$ wt%, (3) $[E]=0.18$ wt%, and (4) $[E]=0.24$ wt%.

Fig. 8 Decrease of the relative tensile strength $\sigma_{B,r}/\sigma_{B,0}$ (○) and weight W_r/W_0 (●) for the undrawn PCL fiber degraded at 25.0°C and pH 7.0 in 0.1M PBS as a function of free LPL degradation time (h): $[E]=0.10$ wt%, $\sigma_{B,0}=600$ g.

of PCL fiber upon enzymatic degradation by free LPL and MAMEC-LPL, respectively, being compared with the weight loss for the undrawn PCL fibers. Both parameters, are expressed relative to those before enzymatic degradation, $\sigma_{B,r}/\sigma_{B,0}$ and W_r/W_0 . As seen in Fig. 8, the curve of decrease of tensile strength does not fit the weight loss curves. If the enzymatic degradation of the PCL fibers results solely in the decrease in the fiber diameter, these two curves theoretically should fit each other. Numerous possible factors account for the poor fitting, such as defects generated during enzymatic degradation. A small defect has large effect on

the strength of fibers but small effect on fiber weight. Undrawn PCL fibers lost mechanical properties faster than their weight loss, as seen in Fig. 8. This might be caused by tensile strength being as more sensitive measure of the extent of degradation than weight loss, because failure occurs at cracks or stress concentration points.

On the other hand, Fig. 9 illustrates that the weight loss of the PCL fibers in the course of MAMEC-LPL digestion take place practically in parallel with the strength loss of the PCL fibers, even though the strength loss take place at a slightly higher rate than

Fig. 9 Decrease of the relative tensile strength $\sigma_{B,r}/\sigma_{B,o}$ (○) and weight W_r/W_o (●) for the undrawn PCL fiber degraded at 25.0°C and pH 7.0 in 0.1M PBS as a function of MAMEC-LPL degradation time (h): ([E]=0.06 wt%, $\sigma_{B,o}$ =600g)

Fig. 10 Decrease of the relative tensile strength $\sigma_{B,r}/\sigma_{B,o}$ (○) and weight W_r/W_o (●) for the drawn PCL fiber (DR=7.0) degraded at 25.0°C and pH 7.0 in 0.1M PBS as a function of free LPL degradation time (h): ([E]=0.10 wt%, $\sigma_{B,o}$ =2450g)

the weight loss of the PCL fibers. This fact suggests again that the degradation of PCL fibers takes place almost only the surface region because of the steric hindrance brought about by fixation of a water-soluble macromolecules MAMEC. To understand the crystallinity of PCL fibers in enzymatic degradation, similar tests were carried out for the drawn PCL fiber (DR=7) as shown in Table 1. Experimental data of decrease of the relative tensile strength and weight loss for the drawn PCL fibers are shown in Fig. 10 and 11, respectively. The initial rate of enzymatic degradation of the undrawn PCL fiber by free LPL is estimated to be more than 2.3 times faster than that the drawn PCL (DR=7) with the same LPL concentration probably due to lower crystallinity. This suggests that the enzymes attack preferentially an amorphous or less-ordered region over a crystalline or more-ordered regions because the enzymes migrate more readily into the less-ordered regions than more-ordered regions.

Fig. 11 illustrates the result obtained with the similar tests by MAMEC-LPL. Again the same behavior was obtained for the drawn PCL (DR=7) that the weight loss of PCL fibers took place almost in parallel with the strength loss of PCL fibers.

4. Conclusion

PCL fibers were enzymatic degraded by LPL modified with MAMEC (MAMEC-LPL) *in vitro*. The degradation of PCL fibers by MAMEC-LPL was assessed by

Fig. 11 Decrease of the relative tensile strength $\sigma_{B,r}/\sigma_{B,o}$ (○) and weight W_r/W_o (●) for the drawn PCL fiber (DR=7.0) degraded at 25.0°C and pH 7.0 in 0.1M PBS as a function of MAMEC-LPL degradation time (h): ([E]=0.06 wt%, $\sigma_{B,o}$ =2450g)

the weight loss and ultimate tensile strength loss. The experimental results were compared with those obtained with free LPL. It was suggested from a kinetic study on weight loss of the PCL fibers with enzymatic degradation by free LPL as well as MAMEC-LPL that degradation generally proceeded gradually from the surface of fiber into the core. While the strength loss took place at a fairly higher rate than the weight loss of PCL fibers in the course of free LPL digestion, the weight loss of PCL fibers in the course of MAMEC-LPL digestion took place practically in parallel with the strength loss of PCL fibers. The degradation of

PCL fibers was found to depend on the crystallinity of PCL fibers, being depressed with increasing crystallinity by drawing.

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<研究論文>

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コポリ(メチルビニルエーテル/無水マレイン酸)修飾リポ蛋白リパーゼによるポリ(ヘキサノー6-ラクトン)繊維の酵素分解

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要 旨

水溶性高分子担体として、コポリ(メチルビニルエーテル/無水マレイン酸)(MAMEC)を選択し、それにリポ蛋白リパーゼ(LPL)を共有結合で修飾させて得られる水溶性高分子修飾リポ蛋白リパーゼ(MAMEC-LPL)によるポリ(ヘキサノー6-ラクトン)(PCL)繊維の酵素分解特性について、酵素分解に伴うPCL繊維の乾燥重量減少率および抗張力低下の度合いを測定することから検討し、未修飾LPLの場合との比較を行った。未修飾LPLによるPCL繊維の分解は、当初、繊維表面から進行するが、酵素分解の進行に伴い、繊維の抗張力低下の度合いは重量減少率よりも速やかに進行した。これは、酵素分解の進行に伴い、酵素分子が次第に繊維内部へも侵入することを示唆した。一方、修飾LPLの場合には、酵素活性そのものは未修飾LPLに比較して僅かに低下するが、酵素分解によるPCL繊維の重量減少に伴う抗張力低下の度合いが効果的に抑制され、繊維表面のみでの分解がかなり長期にわたって維持された。これは、水溶性高分子担体の嵩高さとPCL繊維表面層との相互作用に基づくものと考えられる。また、PCL繊維の延伸処理により、繊維配向性および結晶性が向上すると、酵素分解速度が顕著に低下することが明らかとなった。

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