

## Effects of *In Vitro* Degradation on the Weight Loss and Tensile Properties of PLA/LPCL/HPCL Blend Fibers

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**Abstract:** PLA/LPCL/HPCL blend fibers composed of poly (lactic acid) (PLA), low molecular weight poly ( $\epsilon$ -caprolactone) (LPCL), and high molecular weight poly ( $\epsilon$ -caprolactone) (HPCL) were prepared by melt blending and spinning for bioabsorbable filament sutures. The effects of blending time and blend composition on the X-ray diffraction patterns and tensile properties of PLA/LPCL/HPCL blend fibers were characterized by WAXD and UTM. In addition, the effect of *in vitro* degradation on the weight loss and tensile properties of the blend fibers hydrolyzed during immersion in a phosphate buffer solution at pH 7.4 and 37 °C for 1-8 weeks was investigated. The peak intensities of PLA/LPCL/HPCL blend fibers in X-ray diffraction patterns decreased with an increase of blending time and LPCL contents in the blend fibers. The weight loss of PLA/LPCL/HPCL blend fibers increased with an increase of blending time, LPCL contents, and hydrolysis time while the tensile strength and modulus of the blend fibers decreased. The tensile strength and modulus of the blend fibers were also found to be increased with an increase of HPCL contents in the blend fibers. The optimum conditions to prepare PLA/LPCL/HPCL blend fibers for bioabsorbable sutures are LPCL contents of 5 wt%, HPCL contents of 35 wt%, and blending time of 30 min. The strength retention of the PLA/LPCL/HPCL blend fiber prepared under optimum conditions was about 93.5 % even at hydrolysis time of 2 weeks.

**Keywords:** PLA, LPCL, HPCL, Bioabsorbable sutures, Hydrolysis

### Introduction

A typical application of fibrous materials in biomedical science is as suture materials for closing surgical wounds [1]. Two synthetic biodegradable polymers have been a great deal of interest as bioabsorbable suture materials. They are poly(lactic acid) (PLA) and poly( $\epsilon$ -caprolactone) (PCL). PLA and PCL are aliphatic polyesters that have displayed much promise as materials for bioabsorbable sutures or controlled release of drugs, etc., due to their biocompatibility and degradability [2-5]. Especially, it is well known that PLA has unique physical properties such as enhanced solubility in common organic solvents, easy manufacturing below 200 °C, and no toxicity during degradation [6-8]. However, PLA has some shortcomings such as high crystallinity and resistance against hydrolysis due to hydrophobic methyl groups, etc. These properties restricted the formation of flexible polymer for use as an artificial bone, a muscle, and a bioabsorbable suture [9,10]. On the other hand, PCL is a non-toxic polymer and compatible with other polymers. It can be used as a modifying material for other polymers in blends because it lowers modulus and softens polymers [11-16].

Some efforts have been carried out to improve the miscibility and physical properties between PLA and PCL [17,18]. Nevertheless, they have not been satisfactorily solved yet. In practical, the requirements for a suture material depend on some extent on the type of wound to be closed. It is very important that the bioabsorbable suture must, in any case, retain adequate tensile strength over the critical period of

wound healing. In our previous papers, we have studied the miscibility and the ester interchange reaction by alcoholysis between PLA and low molecular weight poly( $\epsilon$ -caprolactone) (LPCL) [19]. In order to improve the tensile properties of PLA/PCL blends, we have attempted the preparation of PLA/LPCL/HPCL blend fibers by using high molecular weight poly ( $\epsilon$ -caprolactone) (HPCL) [20]. The aims of the present work are to prepare PLA/LPCL/HPCL blend fibers for bioabsorbable filament sutures and to investigate the effect of *in vitro* degradation on the weight loss and tensile properties such as tensile strength and modulus, and strength retention of the blend fibers hydrolyzed during immersion in a phosphate buffer solution at pH 7.4 and 37 °C for 1-8 weeks.

### Experimental

#### Materials

PLA of weight average molecular weight of 85000 (Shimadzu Co.), LPCL of weight average molecular weight of 2000 (Union Carbide Co.), and HPCL of weight average molecular weight of 80000 (Union Carbide Co.) were used.

#### Preparation of PLA/LPCL/HPCL Blend Fibers

PLA and PCL polymers were dried at 40 °C for 48 h *in vacuo* before melt blending. PLA/LPCL/HPCL blends with different compositions were prepared by using an internal mixer (Brabender Co.) at 220 °C with different blending time from 30 to 60 min under screw speed 50 rpm. The composition ratios of PLA/LPCL/HPCL blends were 60/5/35, 60/10/30, 60/15/25, and 60/20/20. Melt spinning to prepare PLA/LPCL/HPCL blend fibers was carried out on a capillary rheometer

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equipped with a 1.2 mm die (L/D 30). The blend fibers quenched to room temperature. The processing conditions for melt spinning are as follows : the plunger speed of 20 mm/min, the drawdown ratio of 200, the heating zone temperature of 200 °C, and the distance between spinning nozzle and take-up roller of 10 cm were used.

### Characterization

Wide angle X-ray diffraction (WAXD) measurements were carried out at room temperature using a diffractometer (MacScience MX18) operated at 45 kV, 200 mA. The diffraction scans were collected at the  $2\theta$  value of between 10 ° and 35 °. The PLA/LPCL/HPCL blend fibers were hydrolyzed in a phosphate buffer solution at pH 7.4 and 37 °C for 1-8 weeks. After hydrolysis the blend fibers were washed with distilled water thoroughly and dried at 40 °C for 48 h *in vacuo*. The *in vitro* degradation behaviors according to hydrolysis were evaluated from the weight loss measurement. The weight loss of the blend fibers was monitored at one week interval over 8 weeks. It was calculated using the following equation:

$$\text{Weight loss (\%)} = (A - B)/A \times 100 \quad (1)$$

Where *A* is the weight of the dried sample before hydrolysis, *B* is the weight of the dried sample after hydrolysis. Tensile properties such as tensile strength and modulus were measured using a UTM (Lloyd Instrument LR 10K). The load cell, the gauge length, and the cross head speed were 500 N, 25 mm, and 10 mm/min, respectively. The strength retention was used to determine the reduction rates of tensile strength of the blend fibers hydrolyzed with different hydrolysis time.

### Results and Discussion

Figure 1 shows the WAXD patterns of PLA, LPCL, and HPCL polymers. The unit cell of PLA is pseudo-orthorhombic with dimensions of  $a = 10.7$ ,  $b = 6.45$ ,  $c = 27.8$  Å and  $\alpha = \beta = \gamma = 90^\circ$ , and the peaks located around  $2\theta = 16.6$  and  $18.9^\circ$  were observed. Also, the unit cells of LPCL and HPCL are orthorhombic with dimensions of  $a = 7.45$ ,  $b = 4.98$ ,  $c = 17.5$  Å, and the peaks located around  $2\theta = 21.4$  and  $23.7^\circ$  were observed [21].

Figure 2 shows the WAXD patterns of PLA/LPCL/HPCL blend fibers prepared with different blending time of 30, 40, 50, and 60 min and various blend compositions of (a) 60/5/35, (b) 60/10/30, (c) 60/15/25, and (d) 60/20/20 wt% .

In Figure 2, the  $2\theta$  values of PLA, LPCL, and HPCL were similar to those observed in Figure 1. However, in Figures 2(a), (b), (c), and (d), as blending time increased from 30 to 60 min, the peak intensities of PLA, LPCL, and HPCL in PLA/LPCL/HPCL blend fibers gradually decreased. Also, in Figure 2(a), (b), (c), and (d), as LPCL contents increased from 5 to 20 wt% and HPCL contents decreased from 35 to 20 wt%, the peak intensities of PLA, LPCL, and HPCL in the blend fibers gradually decreased and the diffraction

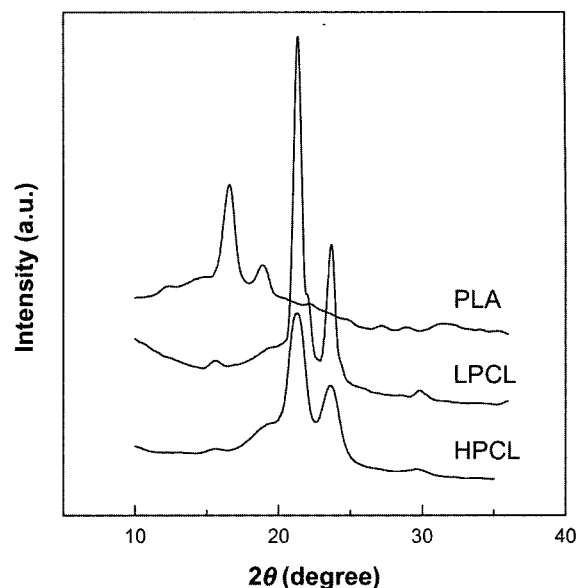


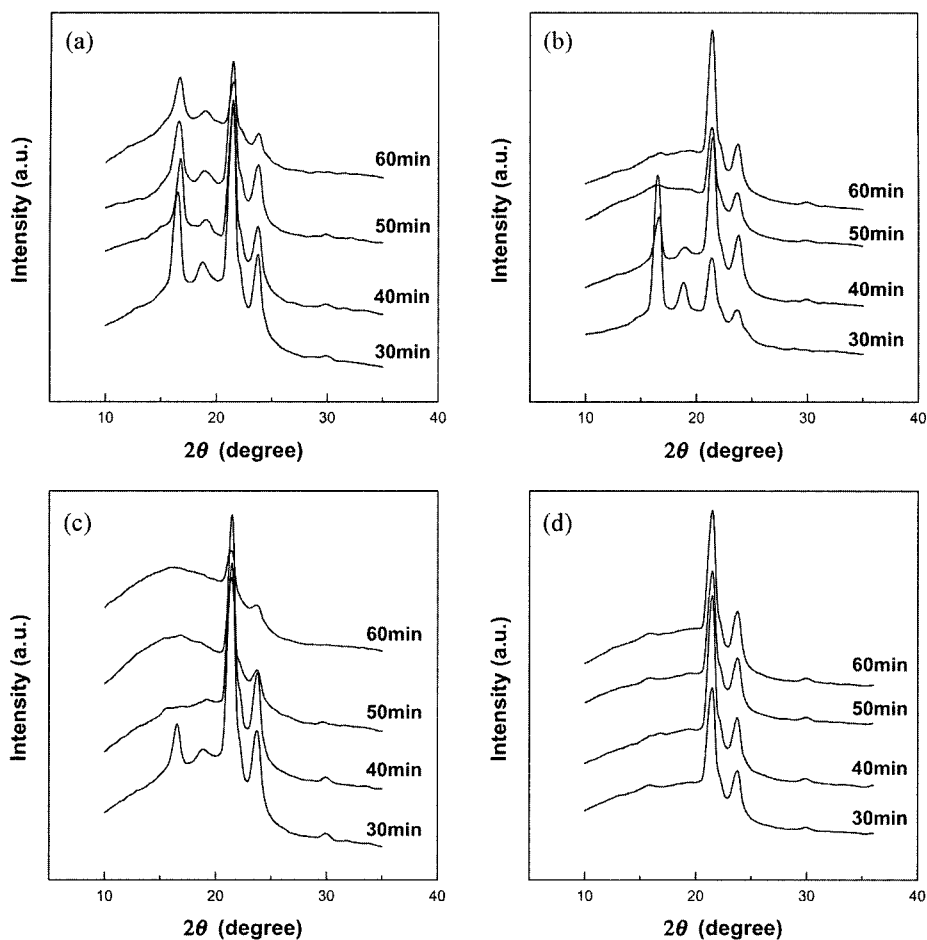
Figure 1. WAXD patterns of PLA, LPCL, and HPCL.

peaks of them became very weak and broad like amorphous patterns. This is because the degree of ester interchange reaction among PLA, LPCL, and HPCL has an influence on the crystallization of PLA/LPCL/HPCL blend fibers [20]. Accordingly, it can be explained that the crystallinity and the peak intensity of the blend fibers through the ester interchange reaction during the melt blending were decreased with an increase of blending time and LPCL contents.

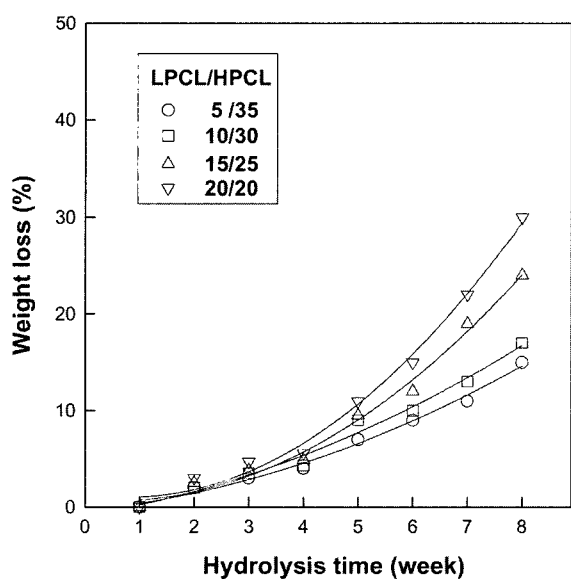
On the other hand, it is well known that the degradation of polymers is a very complicated process, and the rate of degradation is generally affected by chemical composition, crystallinity, water absorption, and chain scission [11]. In this study, the degree of hydrolytic degradation was evaluated from the weight loss measurement.

Figure 3 shows the effects of PCL contents and hydrolysis time on the weight loss of PLA/LPCL/HPCL blend fibers hydrolyzed in the buffer solution at 37 °C and pH 7.4 for various periods of time.

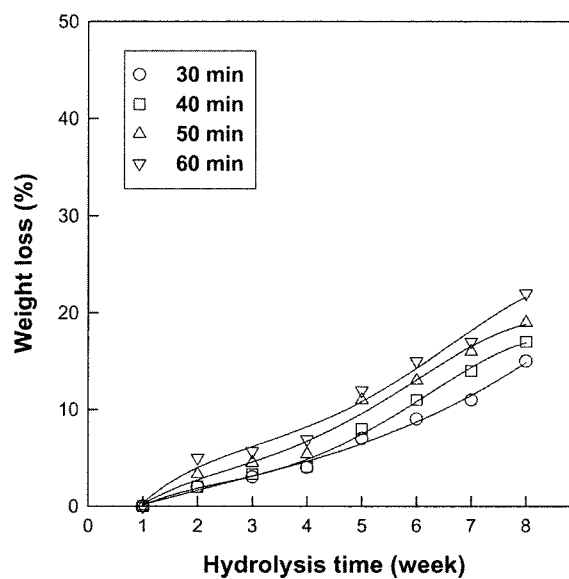
In Figure 3, as LPCL contents increased from 5 to 20 wt% and HPCL contents decreased from 35 to 20 wt% in the blend fibers, the weight loss increased. This is because the degradation rate of LPCL is relatively more rapid than that of HPCL. In addition, the weight loss of the blend fibers was not almost changed at hydrolysis time of one week. However, as hydrolysis time increased from 2 to 8 weeks, the weight loss of the blend fibers gradually increased. This figure also indicates that all the blend fibers show very small increases (below 5 %) in the weight loss after immersion in the buffer solution up to 4 weeks. After increasing slowly at an initial stage, the weight loss increased about 15-30 % at hydrolysis time of 5-8 weeks immersion. Figure 4 shows the effect of hydrolysis time on the weight loss of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time (for 30,



**Figure 2.** WAXD patterns of PLA/LPCL/HPCL blend fibers with different blending time and blend compositions: (a) 60/5/35, (b) 60/10/30, (c) 60/15/25, and (d) 60/20/20 wt%.



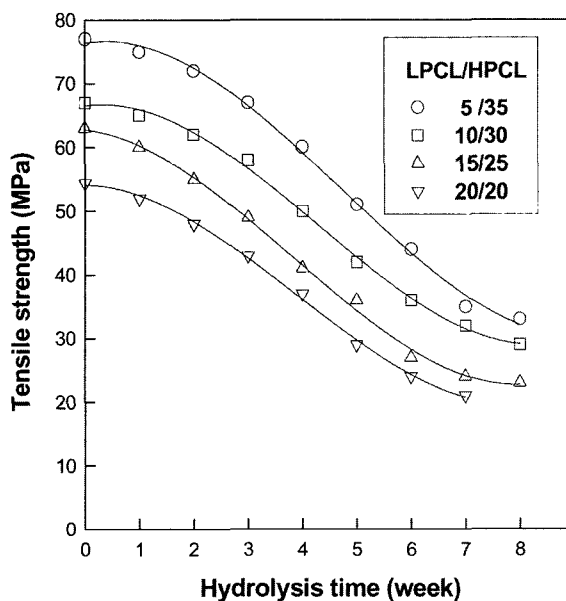
**Figure 3.** Effects of PCL contents and hydrolysis time on the weight loss of PLA/LPCL/HPCL blend fibers (PLA: 60 wt% const., blending time: 30 min).



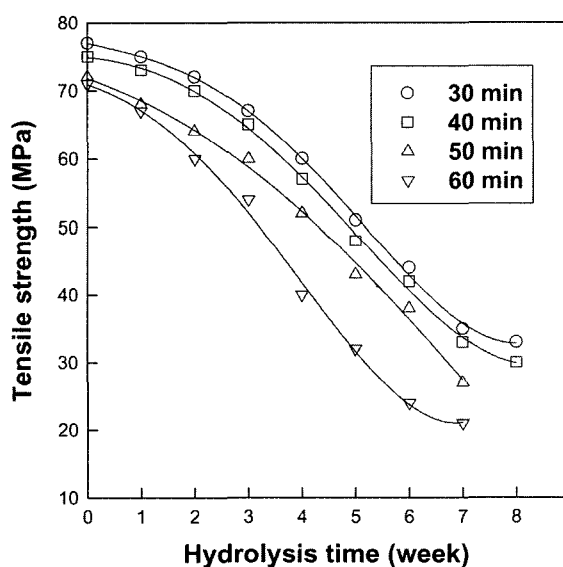
**Figure 4.** Effect of hydrolysis time on the weight loss of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time.

40, 50, and 60 min). In Figure 4, as blending time increased from 30 to 60 min and hydrolysis time increased from 2 to 8 weeks, the weight loss of the blend fibers slowly increased. However, the weight loss of the blend fibers during the first week of immersion in the buffer solution did not change at all.

Figure 5 shows the effects of PCL contents and hydrolysis time on the tensile strength of PLA/LPCL/HPCL blend fibers hydrolyzed in the buffer solution. As HPCL contents increased



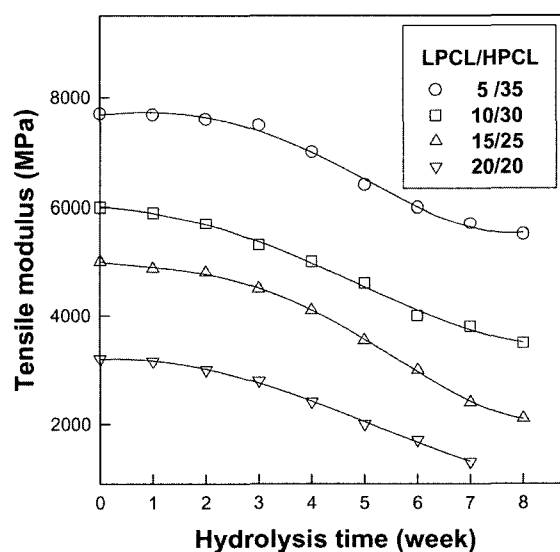
**Figure 5.** Effects of PCL contents and hydrolysis time on the tensile strength of PLA/LPCL/HPCL blend fibers (PLA: 60 wt% const., blending time: 30 min).



**Figure 6.** Effect of hydrolysis time on the tensile strength of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time.

from 20 to 35 wt% and LPCL contents decreased from 20 to 5 wt% in the blend fibers, the tensile strength increased by about 42 %. However, as hydrolysis time increased from 3 to 8 weeks, the tensile strengths of the blend fibers rapidly decreased. Especially, the tensile strengths of the blend fibers hydrolyzed for 1-2 weeks decreased by about 2.6-6.5 %. Figure 6 shows the effect of hydrolysis time on the tensile strength of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time (for 30, 40, 50, and 60 min). As blending time increased from 30 to 60 min and hydrolysis time increased from 3 to 7 weeks, the tensile strengths of the blend fibers greatly decreased. At hydrolysis time of 8 weeks and blending time of 50 and 60 min, the tensile strength measurements of the blend fibers were impossible because of their drastic degradations.

Figure 7 shows the effects of PCL contents and hydrolysis time on the tensile modulus of PLA/LPCL/HPCL blend fibers hydrolyzed in the buffer solution. As HPCL contents increased from 20 to 35 wt% and LPCL contents decreased from 20 to 5 wt% in the blend fibers, the tensile modulus increased by about 175 %. However, as hydrolysis time increased from 3 to 7 weeks, the tensile modulus of the blend fiber decreased by about 28.6-64.3 %. Especially, the tensile modulus at hydrolysis time of 1-2 weeks decreased by about 2-7 %. At hydrolysis time of 8 weeks, the tensile modulus of PLA/LPCL/HPCL (60/20/20 wt%) blend fiber was difficult to measure by using a UTM. Figure 8 shows the effect of hydrolysis time on the tensile modulus of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time (for 30, 40, 50, and 60 min). In Figure 8, as blending time increased from 30 to 60 min and hydrolysis time increased from 3 to 7 weeks, the tensile modulus of the blend fiber rapidly decreased. However,



**Figure 7.** Effects of PCL contents and hydrolysis time on the tensile modulus of PLA/LPCL/HPCL blend fibers (PLA: 60 wt% const., blending time: 30 min).

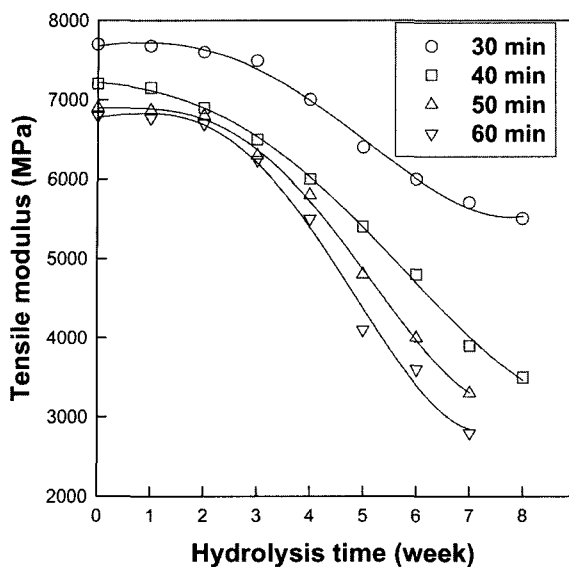


Figure 8. Effect of hydrolysis time on the tensile modulus of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time.

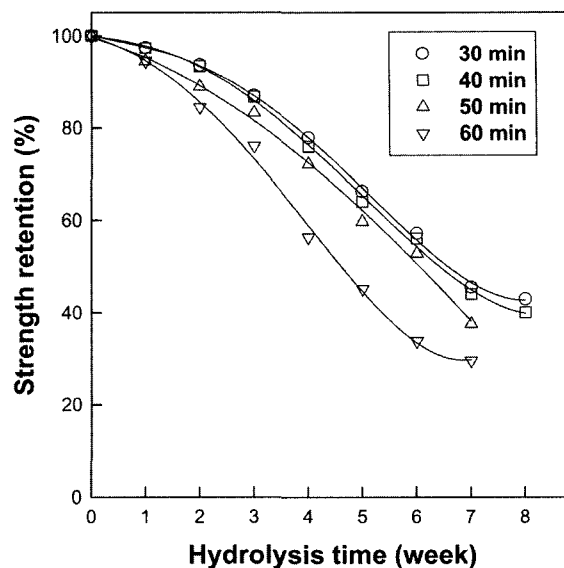


Figure 10. Effect of hydrolysis time on the strength retention of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time.

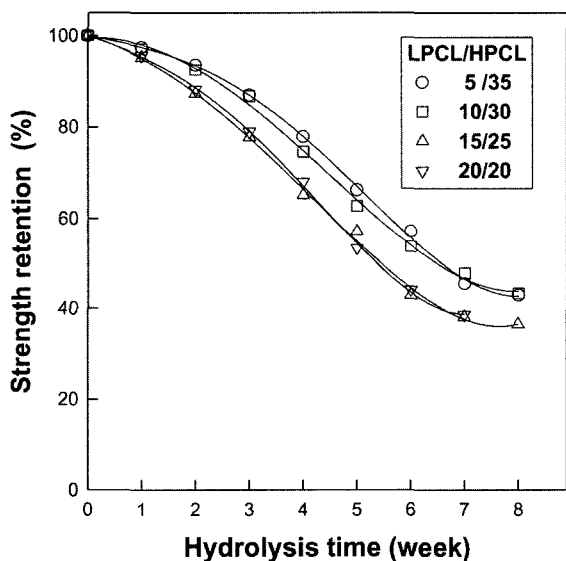


Figure 9. Effects of PCL contents and hydrolysis time on the strength retention of PLA/LPCL/HPCL blend fibers (PLA: 60 wt% const., blending time: 30 min).

at hydrolysis time of 1-2 weeks, the tensile modulus of the blend fiber slightly decreased about below 6 %.

Figure 9 shows the effects of PCL contents and hydrolysis time on the strength retention of PLA/LPCL/HPCL blend fibers hydrolyzed in the buffer solution. As LPCL contents increased from 5 to 20 wt% and HPCL contents decreased from 35 to 20 wt% in the blend fibers, the strength retentions of the blend fibers slightly decreased. Also, as hydrolysis time increased from 1 to 8 weeks, the strength retentions of

the blend fibers rapidly decreased. Figure 10 shows the effect of hydrolysis time on the strength retention of PLA/LPCL/HPCL (60/5/35 wt%) blend fibers with different blending time (for 30, 40, 50, and 60 min). As blending time increased from 30 to 60 min and hydrolysis time increased from 3 to 7 weeks, the strength retentions of the blend fibers rapidly decreased. However, at hydrolysis time of 1-2 weeks, the strength retentions of the blend fibers appeared about 97.4-93.5 %.

From the results of Figure 9 and 10, it can be concluded that the strength retention of PLA/LPCL/HPCL (60/5/35 wt%) blend fiber was significantly appeared about 93.5 % at hydrolysis time of 2 weeks considering that the critical period of wound healing in a surgical operation was about 2 weeks [22].

### Conclusions

The various PLA/LPCL/HPCL blend fibers for bioabsorbable filament sutures were prepared by melt blending and spinning. The effect of *in vitro* degradation on the weight loss and tensile properties of PLA/LPCL/HPCL blend fibers through hydrolysis during immersion in a phosphate buffer solution at pH 7.4 and 37 °C for 8 weeks was investigated. The weight loss, tensile strength and modulus of the blend fibers decreased with increasing hydrolysis time. However, the weight loss, tensile strength and modulus of the blend fibers at hydrolysis time of 2 weeks decreased by about below 7 %. Therefore, The optimum conditions to prepare PLA/LPCL/HPCL blend fibers for bioabsorbable sutures are LPCL contents of 5 wt%, HPCL contents of 35 wt%, and blending time of 30 min. The strength retention of the PLA/LPCL/HPCL blend fiber prepared under optimum conditions was about 93.5 % even

at hydrolysis time of 2 weeks.

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