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The Effects of Blend Composition and Blending Time on the Ester Interchange Reaction and Tensile Properties of PLA/LPCL/HPCL Blends

Cheol Soo Yoon and Dong Sun Ji*

Department of Textile Engineering, Dankook University, Seoul 140-714, Korea

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Abstract: PLA/LPCL/HPCL blends composed of poly(lactic acid) (PLA), low molecular weight poly(ε-caprolactone) (LPCL), and high molecular weight poly(ε-caprolactone) (HPCL) were prepared by melt blending for bioabsorbable filament sutures. The effects of blend composition and blending time on the ester interchange reaction by alcoholysis in the PLA/LPCL/HPCL blends were studied. Their thermal properties and the miscibility due to the ester interchange reaction were investigated by ^{1}H-NMR, DSC, X-ray, and UTM analyses. The hydroxyl group contents of LPCL in the blends decreased by the ester interchange reaction due to alcoholysis. Thus, the copolymer was formed by the ester interchange reaction at 220 °C for 30-60 minutes. The thermal properties of PLA/LPCL/HPCL blends such as melting temperature and heat of fusion decreased with increasing ester interchange reaction levels. However, the miscibility among the three polymers was improved greatly by ester interchange reaction. Tensile strength and modulus of PLA/LPCL/HPCL blend fibers increased with increasing HPCL content, while the elongation at break of the blend fibers increased with increasing LPCL content.

Keywords: Poly(lactic acid), Poly(ε-caprolactone), Melt blending, Ester interchange reaction, Alcoholysis

Introduction

In recent years, there has been a great deal of interest in the use of poly(lactic acid) (PLA) as a plastic material due to its biocompatibility and biodegradability[1,2]. PLA was well recognized as a potential biodegradable polymeric material for medical use in the early 1960s[3]. PLA is known to be a promising material that is suitable for drug delivery system. It is also applied as implants for bone fixation due to its excellent biocompatibility. 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. Because of its biocompatibility, PLA has been widely studied for biomedical applications such as bioabsorbable sutures[4-6].

On the other hand, PLA has some shortcomings such as high crystallinity and resistance against hydrolysis due to hydrophobic methyl groups. These properties disallow the formation of flexible polymer for use as an artificial bone, a muscle, and a bioabsorble sutures[7,8].

Many studies have been carried out to solve the shortcomings of PLA. However, they have not been satisfactorily solved yet. Poly(ε-caprolactone) (PCL) is a non-toxic aliphatic polyester compatible with various polymers[9-11]. Since some efforts have been made to prepare PLA/PCL blends, most studies reported that the immiscibility between PLA and PCL exists[12]. In this regard, it is important to improve the miscibility between PLA and PCL.

In our previous paper, we studied the miscibility and the ester interchange reaction by alcoholysis between PLA and low molecular weight PCL (LPCL)[13]. However, LPCL induced a decrease in tensile properties of PLA/PCL blends. Therefore, it is necessary to increase the tensile properties of PLA/PCL blends. In this regard, the improvement of tensile properties of PLA/PCL blends by using high molecular weight PCL (HPCL) was attempted. It is also significant to explain ester interchange reaction by alcoholysis between PLA and PCL in designing the blend system using LPCL and HPCL together.

In this study, we prepared PLA/LPCL/HPCL blend fibers for bioabsorbable filament sutures and examined the miscibility among PLA, LPCL, and HPCL polymers. Also, the effects of blend composition and blending time on the ester interchange reaction and the tensile properties of PLA/LPCL/HPCL blend fibers were investigated.

Experimental

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. Analytical grade chloroform (Junsei Co.) and deuterated chloroform (Aldrich Co.) were used without any further purification. PLA, LPCL, and HPCL materials were dried in a vacuum oven at 60 °C for at least 48 hrs before melt blending. PLA/LPCL/HPCL blends with different compositions were prepared by using an internal mixer (Brabender Co.) at 220 °C with various blending time from 30 to 60 min under constant screw speed of 50 rpm. The composition ratios of PLA/LPCL/HPCL blends were 60/05/35, 60/10/30, 60/15/25, and 60/20/20.

Melt spinning was carried out on a capillary rheometer

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*Corresponding author: dsunji@dku.edu

equipped with a 1.2 mm die (L/D 30). The monofilament was air cooled. The processing conditions for monofilament 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 nozzle and take-up roller of 10 cm were used. ^{1}H-NMR spectra were obtained using a 200 MHz spectrometer (Varian Gemini). Samples were dissolved in deuterated chloroform. DSC thermograms were obtained using a differential scanning calorimeter (TA Instrument 2100) at a heating rate of 10 °C/min under nitrogen atmosphere. Wide-angle X-ray diffractograms of 10-35° 2θ range were taken with Ni-filtered CuKα radiation using a X-ray diffractometer (MacScience MX18) operated at 45 kV, 200 mA.

Tensile properties such as tensile strength, elongation at break, and tensile modulus were measured using a UTM (Lloyd Instrument LR10K). The load cell, the gauge length, and the cross head speed were 500 N, 25 mm, and 10 mm/min, respectively.

Results and Discussion

Ester Interchange Reaction of PLA/LPCL/HPCL Blends

It is well known that ester interchange reaction such as alcoholysis, acidolysis, and transesterification commonly occur at the melt state in polyester blend system[14-16]. It is generally accepted that alcoholysis occurs during the nucleophilic attack of hydroxyl group that existed as an end-group in polyester chains[17,18].

In Figure 1, the ^{1}H-NMR spectrum of PLA (100 wt%), the CH(A) and the CH_3(B) peaks appeared at 5.15 and 1.58 ppm, respectively. In Figure 2, the ^{1}H-NMR spectra of LPCL (100 wt%) and HPCL (100 wt%) peaks due to CH_2(e), CH_2(a), CH_2(b+d), and CH_2(c) appeared at 4.06, 2.32, 1.65, and 1.41 ppm, respectively. A new peak appeared at 3.65 ppm (e') is due to the methylene connected to the hydroxyl end group of LPCL.

The changes in the ^{1}H-NMR spectra of PLA/LPCL/HPCL blends with different blend compositions (60/05/35, 60/10/30, 60/15/25, and 60/20/20 wt%) are shown in Figure 3. The peaks due to PLA, LPCL, and HPCL polymers appeared around 1.5-1.7 ppm. At blending time of 30 minutes, a new peak due to CH_2(e') appeared at 3.65 ppm. As LPCL contents

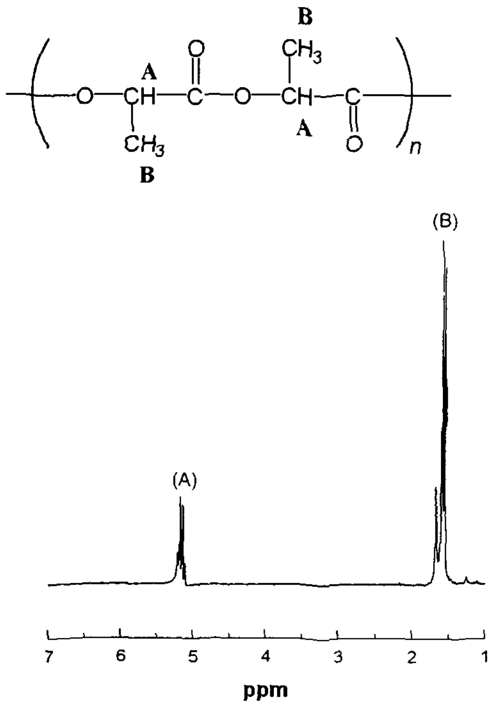

Figure 1. ^{1}H-NMR spectrum of PLA.

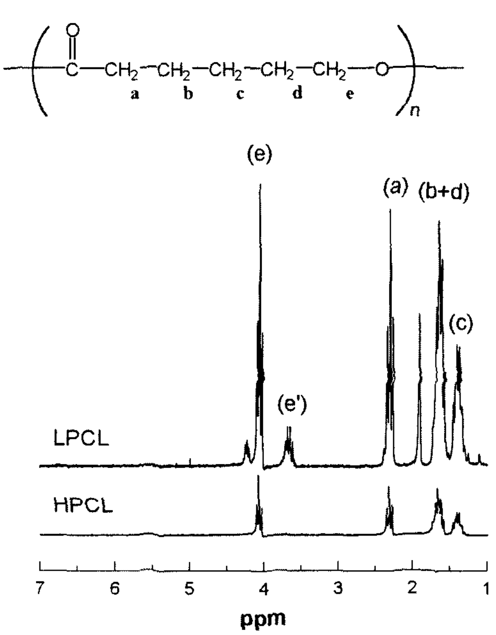

Figure 2. ^{1}H-NMR spectra of LPCL and HPCL.

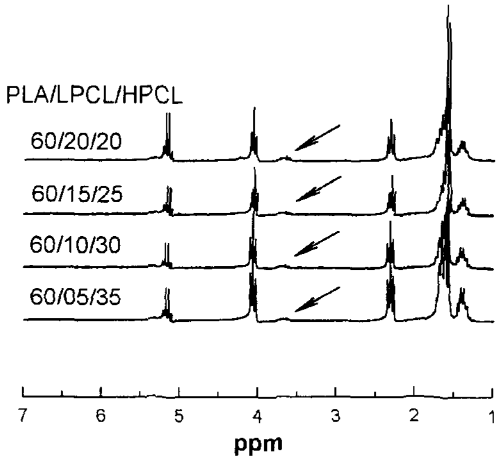

Figure 3. ^{1}H-NMR spectra of PLA/LPCL/HPCL blends with different blend compositions(blending time: 30 min).

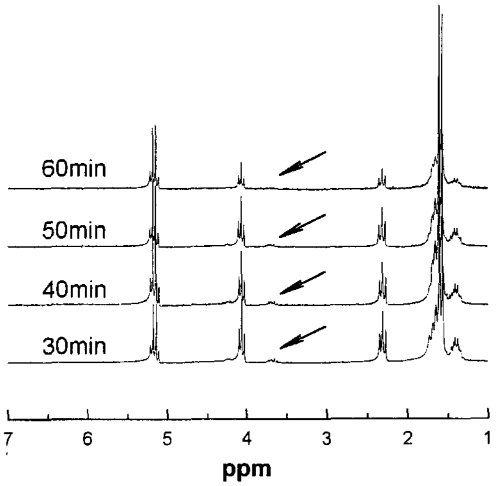

Figure 4. ^{1}H-NMR spectra of PLA/LPCL/HPCL (60/20/20 wt%) blends with different blending time.

had an influence on the peak area of CH_2(e'), the peaks of CH(A) and CH_3(B) due to PLA appeared, and the peaks of CH_2(a, b, c, d, and e) due to LPCL and HPCL appeared, respectively.

Figure 4 is the ^{1}H-NMR spectra of PLA/LPCL/HPCL blends for different blending time (for 30, 40, 50, and 60 min). In Figure 4, as blending time increased from 30 to 60 minutes, the peak due to CH_2(e') becomes small and completely disappeared at 60 min, but the peaks due to PLA and HPCL appeared, respectively. Therefore, from the comparison of CH_2(e') peak of LPCL in Figure 2 with CH_2(e') peak of blends in Figures 3 and 4, it is observed that the peak of CH_2 (e') appeared at 3.65 ppm is not affected by the hydroxyl group as blending time is increased from 30 to 60 minutes.

It is confirmed that the hydroxyl group contents of LPCL is decreased by the ester interchange reaction due to alcoholysis.

On the other hand, in PLA/LPCL/HPCL blends prepared from PLA, LPCL, and HPCL polymers, P(LA-co-CL) copolymers are formed by the ester interchange reaction due to alcoholysis at 220 °C for 30-60 minutes.

The DSC curves of PLA, LPCL, and HPCL polymers are shown in Figure 5. The melting temperatures (Tm) of pure PLA, LPCL, and HPCL polymers are shown at 175, 54, and 63 °C, respectively. The heats of fusion (ΔHm) of pure PLA, LPCL, and HPCL polymers are 68.5, 31.0, and 27.3 J/g, respectively. The glass transition temperature (Tg) of PLA was about 60-65 °C. There, because Tm of PCL and Tg of PLA are similar values, the result was that DSC analysis fail to distinguish between Tm of PCL and Tg of PLA in PLA/LPCL/HPCL Blends.

Figure 6 shows the DSC curves of PLA/LPCL/HPCL blends melt-blended for 30 minutes with different blend compositions (60/05/35, 60/10/30, 60/15/25, and 60/20/20 wt%).

In Figure 6, as LPCL contents increased from 5 to 20 wt% in PLA/LPCL/HPCL blends, the melting temperature due to PLA was decreased by about 2-5 °C. The melting temperature due to HPCL and LPCL in PLA/LPCL/HPCL blends appeared as a single peak at 57-58 °C. Also, the melting temperature due to PCL in PLA/LPCL/HPCL blends decreased by about 2 °C as LPCL contents increased from 5 to 20 wt%. The heat of fusion due to PLA in PLA/LPCL/HPCL blends, as LPCL contents increased from 5 to 20 wt%, decreased by about 18-36 J/g compared with pure PLA. The heat of fusion due to PCL in PLA/LPCL/HPCL blends was slightly decreased as LPCL contents increased from 5 to 10 wt% and 15 to 20 wt%.

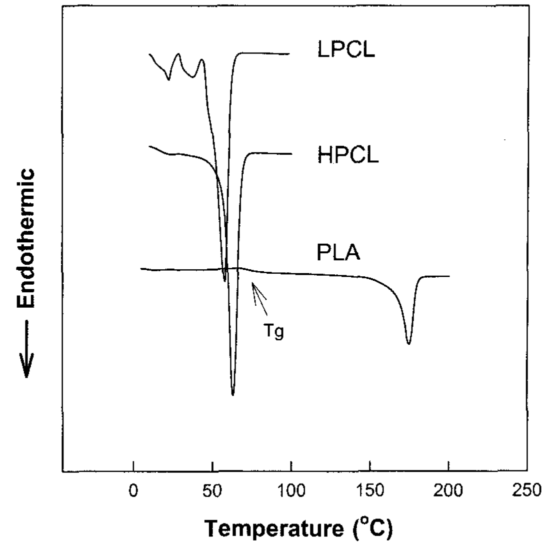

Figure 5. DSC thermograms of PLA, LPCL, and HPCL.

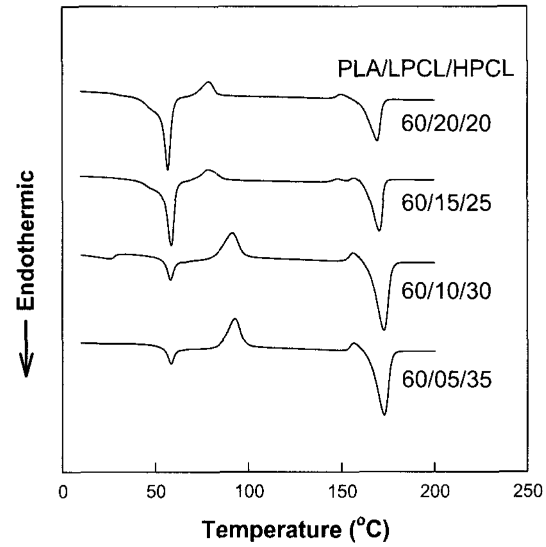

Figure 6. DSC thermograms of PLA/LPCL/HPCL blends with different blend compositions(blending time: 30 min).

The DSC curves of PLA/LPCL/HPCL blends (60/20/20

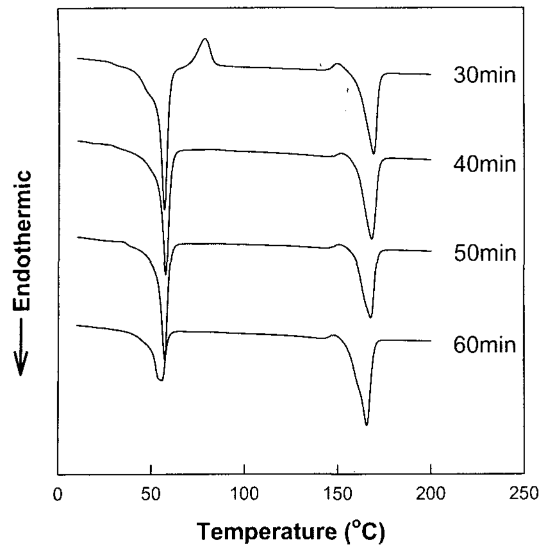

Figure 7. DSC thermograms of PLA/LPCL/HPCL (60/20/20 wt%) blends with different blending time.

Table 1. Melting temperature and heat of fusion of PLA/LPCL/HPCL blends with different blend compositions(blending time: 30 min)

Blend compositions (PLA/LPCL/HPCL wt%)	PLA		LPCL+HPCL	
	Tm (°C)	ΔHm (J/g)	Tm (°C)	ΔHm (J/g)
100/0/0	175.0	68.5		
0/100/0			54.0	31.0
0/0/100			63.0	27.3
60/05/35	172.9	50.6	58.3	7.3
60/10/30	172.0	48.0	58.0	6.9
60/15/25	170.0	46.0	58.0	30.0
60/20/20	169.3	32.4	57.7	29.2

wt%) melt-blended for 30 to 60 minutes are shown in Figure 7. The melting temperature due to PLA in PLA/LPCL/HPCL blends, decreased by about 6-10 °C as blending time increased from 30 to 60 minutes. Also, the melting temperature due to PCL in PLA/LPCL/HPCL blends decreased by about 6 °C as blending time increased from 30 to 60 minutes. The heat of fusion due to PLA in PLA/PCL blends, decreased by about 36.1-41.5 J/g compared with pure PLA as blending time increased from 30 to 60 minutes. Also, the heat of fusion due to PCL in PLA/LPCL/LPCL blends decreased by about 10 J/g as blending time increased from 30 to 60 minutes.

Table 1 shows the results of melting temperature and heat of fusion of PLA/LPCL/HPCL blends with different blend compositions at blending time of 30 minutes. Melting temperature and heat of fusion due to PLA and PCL in PLA/LPCL/HPCL blends, decreased as LPCL contents increased from 5 to 20 wt%.

Table 2. Melting temperature and heat of fusion of PLA/LPCL/HPCL (60/20/20 wt%) blends with different blending time

Blending time (min)	PLA		LPCL+HPCL	
	Tm (°C)	ΔHm (J/g)	Tm (°C)	ΔHm (J/g)
30	169.3	32.4	57.7	29.2
40	168.1	27.3	57.5	28.0
50	167.7	27.3	57.2	28.0
60	165.0	27.0	55.6	19.4

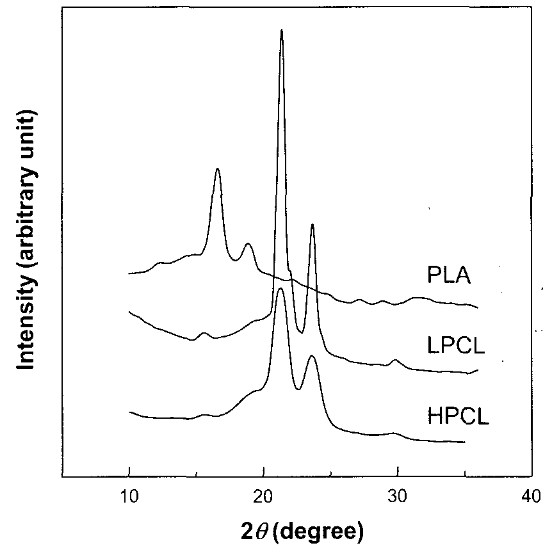

Figure 8. X-ray diffractograms of PLA, LPCL, and HPCL.

Table 2 shows the results of melting temperature and heat of fusion of PLA/LPCL/HPCL (60/20/20 wt%) blends with different blending time. Melting temperature and heat of fusion due to PLA and PCL in PLA/LPCL/HPCL blends, decreased as blending time increased from 30 to 60 minutes.

In the case of PLA/LPCL/HPCL blends prepared from PLA, LPCL, and HPCL, Figures 6 and 7 showed that block copolymer was prepared by the ester interchange reaction due to alcoholysis, because the melting temperature of the blends is slightly reduced. The degree of ester interchange reaction among PLA, LPCL, and HPCL increased with increasing LPCL content and blending time.

Figure 8 shows the X-ray diffraction 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° were observed. Also, the unit cell of PCL is 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° were observed[19].

Figure 9 shows the X-ray diffraction patterns of PLA/LPCL/HPCL blends prepared for 30 min at blend compositions of 60/05/35, 60/10/30, 60/15/25, and 60/20/20

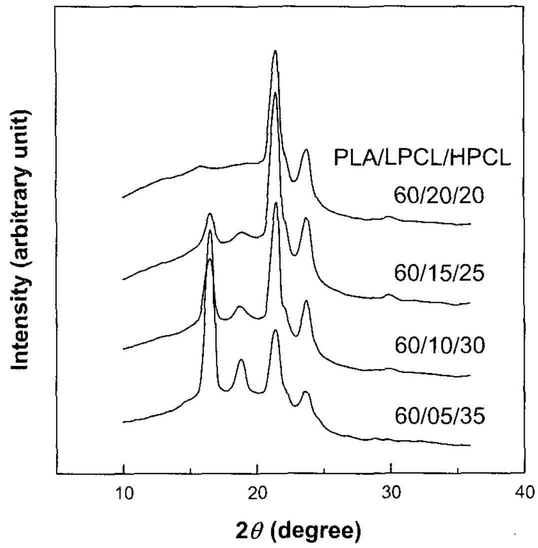

Figure 9. X-ray diffractograms of PLA/LPCL/HPCL blends with different blend compositions(blending time: 30 min).

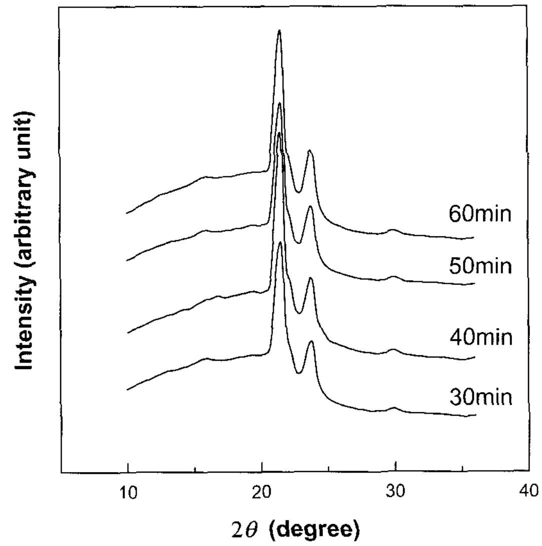

Figure 10. X-ray diffractograms of PLA/LPCL/HPCL (60/20/20 wt%) blends with different blending time.

wt%. The peak intensity due to PLA in PLA/LPCL/HPCL blends gradually decreased as LPCL contents increased from 5 to 20 wt%.

Figure 10 shows the X-ray diffraction patterns of PLA/LPCL/HPCL blends prepared for 30, 40, 50, and 60 min at blend compositions of 60/20/20 wt%. As blending time increased from 30 to 60 minutes, the peaks due to PLA in PLA/LPCL/HPCL blends became very broad and weak. Peaks due to PCL in PLA/LPCL/HPCL blends did not appear around $2\theta = 10\text{-}30^\circ$. Accordingly, the degree of ester interchange reaction influences the crystallization of PLA/LPCL/HPCL blends.

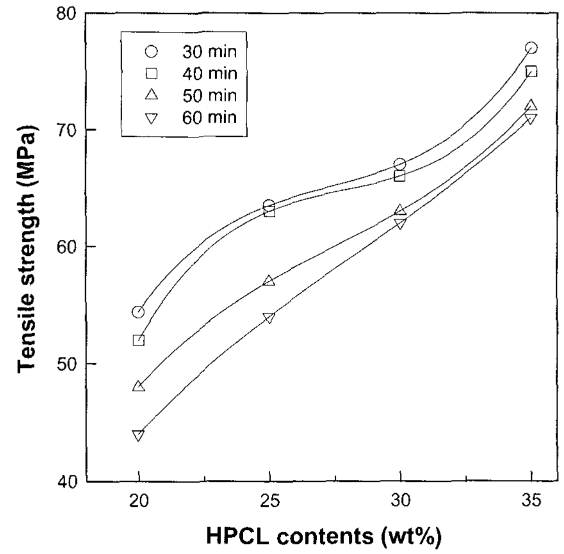

Figure 11. Effects of HPCL contents and blending time on the tensile strength of PLA/LPCL/HPCL blend fibers.

In this regard, it can be concluded that the crystallinity and the peak intensity of the blends decrease with increasing the LPCL contents and blending time.

Tensile Properties of PLA/LPCL/HPCL Blend Fibers

Figure 11 shows the effects of HPCL contents and blending time on the tensile strength of PLA/LPCL/HPCL blend fibers. As HPCL contents increased from 20 to 35 wt% at blending time of 30 minutes, the tensile strength increased by about 42 %. It increased in about 44 % at blending time of 40 minutes, and increased in about 50 % at blending time of 50 minutes. At blending time of 60 minutes, the tensile strength increased by about 61 %. It was assumed that the strength of PLA/LPCL/HPCL blend fibers decreased with increasing amorphous PCL content, but the tensile strength of the blend fibers increased with increasing HPCL contents and decreasing LPCL contents. As a matter of fact, this result is very similar to the fact that polymers having high molecular weight produce the improved physical properties in general.

The effects of LPCL contents and blending time on the elongation at break of PLA/LPCL/HPCL blend fibers are shown in Figure 12. As LPCL content increased from 5 to 20 % at blending time of 30 minutes, the elongation at break increased from about 5.0 to 16.3 %, respectively. At blending time of 40 minutes, it also increased from about 5.5 to 16.7 %, and increased from about 5.8 to 16.9 % at melt blending time of 50 minutes. At blending time of 60 minutes, the elongation at break increased from about 6.0 to 17.2 %. Introduction of LPCL having a flexible chain into PLA have increased the elongation at break of PLA/LPCL/HPCL blend fibers. It is explained by the fact that amorphous region

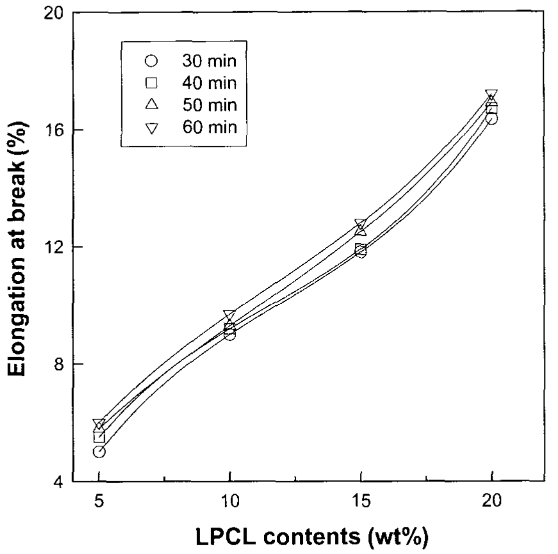

Figure 12. Effects of LPCL contents and blending time on the elongation at break of PLA/LPCL/HPCL blend fibers.

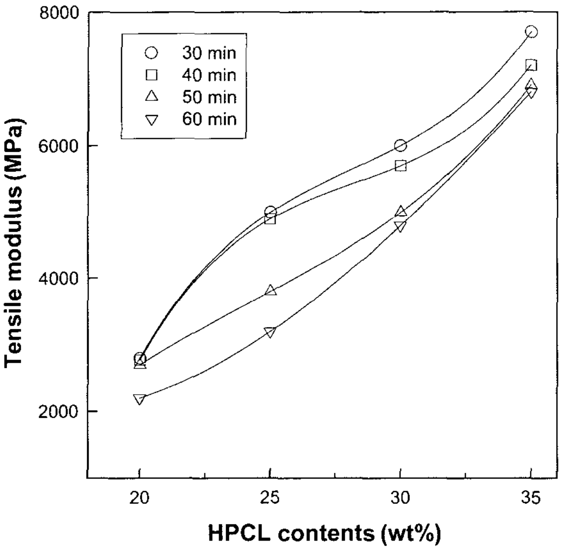

Figure 13. Effects of HPCL contents and blending time on the tensile modulus of PLA/LPCL/HPCL blend fibers.

of the blend fiber is markedly increased with increasing ester interchange reaction. Therefore, it is proved that the brittleness of PLA is improved by introducing PCL to PLA backbone.

Figure 13 shows the effects of HPCL contents and blending time on the tensile modulus of PLA/LPCL/HPCL blend fibers. As HPCL content increased from 20 to 35 wt% at blending time of 30 minutes, the tensile modulus increased from 2800 to 7700 MPa, respectively. At blending time of 40 minutes it increased from 2770 to 7200 MPa. At blending time of 50 minutes, it increased from 2700 to 6900 MPa. At blending time of 60 minutes, the modulus increased from 2200 to 6800 MPa. It is assumed that the tensile strength of the fibers has an influence on the increased tensile modulus. Consequently, it is confirmed that the elongation at break of the blend fibers at less than 20 wt% of LPCL content desirably increased, and the tensile strength and modulus of them at less than 35 wt% of HPCL content significantly increased.

Conclusions

The aliphatic PLA/LPCL/HPCL blends for bioabsorbable filament sutures were prepared by melt blending. The ester interchange reaction by alcoholysis among the three polymers and their tensile properties were investigated.

The PLA/LPCL/HPCL copolymers that were formed during the melt blending through the ester interchange reaction by alcoholysis could be confirmed from the following results. The peak due to CH_2(e') was disappeared at 3.65 ppm, the melting temperature and the heat of fusion due to PLA and PCL in the blends were decreased, and the crystallinity and X-ray peak intensity were decreased. The ester interchange reaction among PLA, LPCL, and HPCL polymers increased with increasing LPCL content (5-20 wt%) and blending time (30-60 min). Tensile strength and modulus of PLA/LPCL/HPCL blend fibers increased with increasing HPCL content, while the elongation at break of the blend fibers increased with increasing LPCL content.

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