IMPROVEMENT OF FLEXURAL STRENGTH OF BIODEGRADABLE POLYMERIC INTERNAL FIXATION DEVICE BY SOLID STATE EXTRUSION

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ABSTRACT

Solid-state extrusion technique was employed for the improvement of mechanical properties of polylactic acid (PLLA) widely used as biodegradable internal fixation devices currently. Cylindrical billets were machined out from the vacuum compression-molded PLLA to have various diameters, and solid-state extrusion of the billets was performed at various drawing rates and at the extrusion temperature of 130°C. Throughout the whole processes the decrease in molecular weight was significantly suppressed to be about 10%. Flexural modulus and strength of PLLA increased up to 8.3 GPa and 221 MPa, respectively. Studies on the orientation and crystallinity of extruded PLLA could reveal the effects of billet morphology, draw ratio, and drawing rate on the flexural strengths of PLLA.

INTRODUCTION

Biodegradable polymeric internal fixation devices have many advantages over metallic or ceramic fixation devices such as good biocompatibility, safe reduction of the fracture due to their progressive transfer of stresses to the healing bone, no corrosion problems, and no need for the second removal operation. Aliphatic polyesters such as PLLA are the most widely used biodegradable polymers and have various applications for the internal fixation devices of lower strength materials, e. g., interference screws in the ankle, knee, and hand; tacks and pins for ligament attachment; rods and pins for bone fracture fixation. However, biodegradable polymers show lower strengths than metallic or ceramic fixation devices and thus are not suitable for the high strength end-uses such as femur. Processing method is another reason for lower strengths for polymeric fixation devices, that is, melt processing accompanies molecular degradation which leads to the decrease in mechanical properties [1].

In this study vacuum compression molding and solid-state extrusion technique [2-5] were employed for the enhancement of mechanical properties of PLLA. Both steps were adopted and designed for the minimization of molecular degradation during the processes. Improved mechanical properties were to be obtained through the development in orientation and crystallinity given by the solid-state extrusion process. From this study relationship among the vacuum compression molding/solid-state extrusion conditions - microstructure - mechanical properties of PLLA could be revealed.

EXPERIMENTAL

PLLA having M_v of 220,000 (Simadzu Ltd.) was used. PLLA was compression molded at 200°C for 2 hours with vacuum condition maintained in the mold. Cooling of the molded PLLA was performed at 10°C/min down to room temperature or to 80°C and placed at room temperature. Cylindrical billets were machined out from the vacuum compression-molded PLLA to have diameters ranging from 11.5 mm to 13.5 mm. Solid-state extrusion of the billets was performed at drawing rates ranging from 40 mm/min to 145 mm/min. The extrusion temperature was set to 130°C. The die had a diameter of 5 mm and an entrance angle of 15°.

Various structural estimations of the extruded PLLA were performed, e. g., DSC, GPC, WAXS, and birefringence. Three point flexural strength tests were done with an Instron tester at room temperature. Sample and span lengths were adjusted at 100 mm and 80 mm, respectively. The crosshead speed was set to 1 mm/min.

RESULTS AND DISCUSSION

Cooling conditions employed herein produced two types of compression molded PLLA which differ in morphology. PLLA compression molded and cooled down to room temperature had little crystallinity of 10%, while PLLA molded, cooled down to 80°C, and placed at room temperature had crystallinity of 30%. For both compression-molded samples M_v had 210,000. This yields a notably small decrease in molecular weight below 5% compared with other studies [4, 5], which implies that vacuum compression molding utilized in this study prevents thermal degradation effectively during the molding process. For both crystallinities brittle fracture occurred at the flexural strain below 0.1.

Under the solid-state extrusion conditions adopted in this study maximum extrudable billet diameter was 13.5 mm. Diameters of the extruded PLLA (D_f) were smaller than the diameter of the die, which implies that further drawing occurred outside the die exit (Table 1). Draw ratio calculated as the ratio of the areas of the billet to the extruded rod ranged from 5.6 – 9.1. Even when the effect of drawing rate was considered at a fixed billet diameter, draw ratio increased with increasing drawing rate. This means that the effect of drawing rate partially transformed to that of the draw ratio. Notwithstanding billet morphology, draw ratio, and drawing rate, all the solid-state extruded PLLA had M_v over 190,000, which leads to the result that the decrease in molecular weight throughout the whole processes was highly suppressed to be about 10%.

Table 1. Sample notation and the calculated draw ratios.

Billet crystallinity (%)	D_b (mm)	Drawing rate (mm/min)	D_f (mm)	Draw ratio
10	11.5 (●)	40	4.85	5.6
	12.0 (▲)	40	4.75	6.4
	12.5 (▼)	40	4.75	7.0
	13.0 (■)	40	4.70	7.7
	13.0 (▩)	75	4.55	8.2
	13.0 (▩)	110	4.32	9.0
	13.0 (▩)	145	4.30	9.1
	13.5 (◆)	40	4.55	8.8
30	11.5 (○)	40	4.85	5.6
	12.0 (△)	40	4.75	6.4
	12.5 (▽)	40	4.75	7.0
	13.0 (□)	40	4.70	7.7
	13.5 (◇)	40	4.55	8.8

D_b: billet diameter; D_f: diameter of the extruded PLLA;
Draw ratio is calculated as D_b^2/D_f^2.

While heated up to the extrusion temperature of 130°C prior to solid-state extrusion, thermally-induced crystallization occurred producing spherulitic crystals. They were transformed into fibrillated crystals during the solid-state extrusion process. With increasing draw ratio, more sharp and resolved PLLA orthorhombic crystalline peaks were obtained in WAXS patterns indicating the formation of more developed crystals (Figure 1). Crystalline orientation also increased as draw ratio increased. In DSC thermograms, no cold-crystallization peak occurred for solid-state extruded PLLA and heat of crystal melting increased with increasing draw ratio. Increase in molecular orientation also occurred during the solid-state extrusion process, and birefringence had higher values at higher billet crystallinity, draw ratio, and drawing rate.

In flexural tests, no brittle fracture occurred and work of rupture increased for solid-state extruded PLLA. As billet crystallinity, draw ratio, and drawing rate increased, both flexural modulus and strength increased. Figure 2 shows the result of flexural strength. (Note the effect of drawing rate is coplotted.) Maximum flexural modulus and strength obtained were 8.3 GPa and 221 MPa, respectively. This is higher than the strength values of cortical bone having flexural modulus of about 7 GPa and flexural strength of 200 MPa. Both flexural modulus and strength increased with increasing crystallinity and birefringence of solid-state extruded PLLA. It was found that the correlation between birefringence and flexural modulus was very good in linear regression results.

CONCLUSIONS

Vacuum compression molding and solid-state extrusion technique were employed for the enhancement of mechanical properties of PLLA. Throughout the whole processes the decrease in molecular weight was effectively suppressed to be about 10%. Flexural

modulus and strength were increased up to 8.3 GPa and 221 MPa, respectively. With increasing billet crystallinity, draw ratio, and drawing rate, both flexural modulus and flexural strength of extruded PLLA increased, which was due to the developments in orientation and crystallinity.

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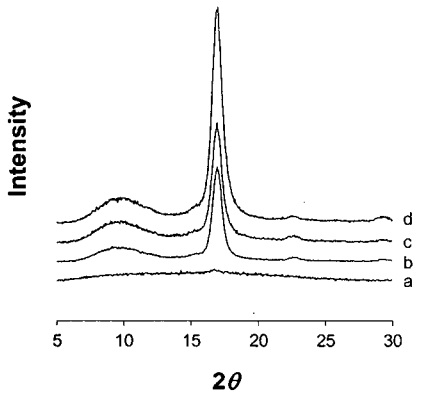

Figure 1. Equatorial WAXS patterns of PLLA billet (crystallinity = 10%) (a) and PLLA solid-state extruded from that billet; D_b's are (b) 11.5, (c) 12.5, and (d) 13.5 mm, respectively.

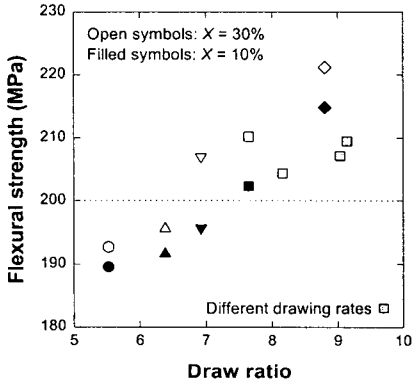

Figure 2. Change in flexural strength of solid-state extruded PLLA as a function of draw ratio.