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Preparation and Properties of Self-reinforced L- and D,L-lactide Copolymer Rods

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Abstract: Since highly crystalline poly (L-lactide) (PLLA) degrades rather slowly in a biological environment and the crystalline domains remaining after partial degradation of the implant material give rise to an inflammatory response of the surrounding tissue, L- and D,L-lactide copolymer [P(L-DL)LA] having a low crystallinity is preferred in surgical applications. The thermal transitions and the mechanical properties of P(L-DL)LA rods were discussed in this paper. It was found that the self-reinforced P(L-DL)LA [SR-P(L-DL)LA] was strong enough in terms of mechanical properties compared with the self-reinforced PLLA [SR-PLLA].

Keywords: PLLA, P(L-DL)LA, self-reinforcement, bone fractures fixation.

Because of its biocompatibility and strong mechanical strength, PLLA has been widely studied for biomedical applications such as devices for bone fractures fixation and body absorbable sutures. However, the degradation time of the PLLA implants is unacceptably long and the crystalline remnants of PLLA can cause a late tissue response, making a removal operation of the remnants of implants necessary[1, 2]. To avoid this negative side effect of PLLA, P(L-DL)LA having a low crystallinity is preferred. In our laboratory, high molecular weight P(L-DL)LA(L:DL=9:1) was synthesized with stannous octoate as initiator and high strength copolymer rods were achieved after extrusion and self-reinforcement. In this communication, the thermal transitions of P(L-DL)LA are discussed and the mechanical properties of the SR-P(L-DL)LA rods were presented and compared with the SR-PLLA materials reported by literatures.

The P(L-DL)LA rods were extruded on Brabebder PLE-330 (Germany) at 155℃. Differential scanning calorimetry (DSC) measurements were conducted with a Netzsch DSC 204 apparatus calibrated with pure indium. X-ray diffraction powder patterns were recorded with a Rigaku D/Max-2500 X-ray apparatus. The mechanical strengths were measured with a Testometric Universal Tester M500-25kN.

Depending on the optical purity of the polylactides, they have different thermal transitions, as reported in the DSC thermograms of **Figure 1**, and summarized in **Table 1**. PLLA shows a high crystallinity of 52.5% and melts at 177℃. P(L-DL)LA exhibits a lower crystallinity of 29.2% and its melting peak appears near 153℃. Poly (D,L-lactide) (PDLLA) is totally amorphous and has no melting peak at all. The difference of the melting point between PLLA and P(L-DL)LA suggests another advantage of P(L-DL)LA that it can be processed under relatively low temperatures so as to lighten the degree of thermal degradation during the processing.

Figure 1 DSC thermograms of solution-precipitated polylactides having different optical purities

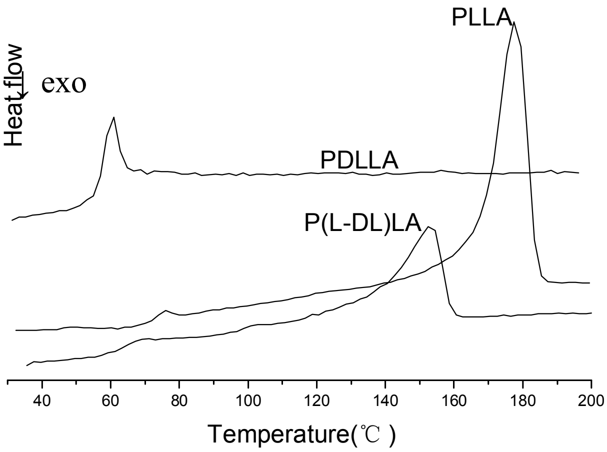

Table 1 Physicochemical data of solution-precipitated polylactides having different optical purities

Sample	M_w ($\times 10^4$)	T_g (℃)	T_m (℃)	ΔH_c (J/g)	ΔH_m (J/g)	Crystallinity* (%)
PLLA	30.7	72.3	177	-	48.9	52.5
P(L-DL)LA	32.1	61.9	153	-	27.2	29.2
PDLLA	17.6	56.9	-	-	-	-

*The crystallinity is calculated according to reference 3

Table 2 Mechanical properties of P(L-DL)LA rods

Manufacturing Method[a]	Rods diameter (mm)	Tensile strength[c] (MPa)	Elastic modulus (GPa)	Bending strength[d] (MPa)	Bending modulus (GPa)	Shear strength[e] (MPa)
undrawn[b]	3.2	59.9	1.8	147	2.8	151
orientation (λ =2)	1.8	77.8	1.0	147	4.0	146
orientation (λ =5)	1.4	233	1.5	165	4.7	162
orientation (λ =7)	1.2	329	1.6	237	8.8	157

a The orientation occurs under directional mechanical stress at 90℃ and is fixed by quenching to room temperature; b $M_w=9.3\times 10^4$; c Test speed=20.00mm/min, sample length=25.0mm, sample type: circular; d Test speed=10.00mm/min, support span: 38mm; e Test speed=10.00mm/min

Table 2 reports the mechanical properties of P(L-DL)LA rods extruded at 155℃ and drawn at 90℃ to various drawing ratios. It can be clearly seen that the strength properties, including tensile strength, bending strength, and bending modulus, improve significantly as the drawing ratio(λ) increases. The self-reinforcement does not give much improvement to the shear strength of P(L-DL)LA rods because the shear strength measurement arrangement used in the present study measures the shear effect in the direction perpendicular to the orientation axis of the rod.

As shown in **Table 3**, the crystallinity of P(L-DL)LA increases with the degree of orientation, due to the stress-induced crystallization effect.

Table 3 DSC analysis of P(L-DL)LA rods

Sample No.	Manufacturing Method*	T_g (℃)	T_m (℃)	ΔH_c (J/g)	ΔH_m (J/g)	Crystallinity (%)
1	undrawn**	60.0	151	-	8.6	-
2	orientation (λ =2)	61.0	146	-4.4	25.2	22.4
3	orientation (λ =5)	62.1	147	-1.1	28.8	29.1
4	orientation (λ =7)	69.1	146	0	29.3	31.5

* The orientation occurs under directional mechanical stress at 90℃ and is fixed by quenching to room temperature;

** $M_w=9.3\times10^4$

Figure 2 X-ray diffraction curves of PLLA, SR-P(L-DL)LA rod (λ =7) and P(L-DL)LA rod (undrawn)

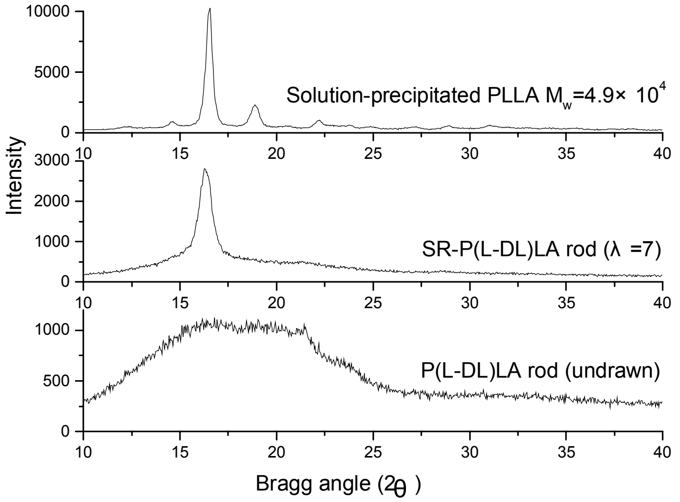

Figure 2 gives the X-ray diffraction curves of solution-precipitated PLLA, SR-P(L-DL)LA rod (λ =7) and P(L-DL)LA rod (undrawn). The undrawn rod has merely amorphous scattering because of the absence of the orientation. PLLA shows its most intense peas at 2 θ values of 14.6, 16.5, 18.9 and 22.2, in agreement with the peaks reported by Sarasua *et al*[4]. As for SR-P(L-DL)LA rod (λ =7), only one main peak is observed at 2 θ equal to 16.5. Comparing the X-ray diffraction curve of PLLA and that of SR-P(L-DL)LA, we assume that the self-reinforcement of P(L-DL)LA causes the preferred orientation of crystallites so that the crystal planes at the 2 θ values of 14.6, 18.9 and 22.2 can not be detected.

The mechanical strength data of SR-PLLA reported by literatures are given in **Table 4**. SR-P(L-DL)LA is a suitable candidate for the fixation of bone fractures in terms of mechanical properties as a result of the comparison.

Table 4. Mechanical properties of SR-P(L-DL)LA and SR-PLLA cylindrical rods

Author(year)	Material	Rods diameter (mm)	Tensile strength (MPa)	Bending strength (MPa)	Bending modulus (GPa)	Shear strength (MPa)
In our laboratory	SR-P(L-DL)LA	1.2	329	237	8.8	157
Tormala (1990)[5]	SR-PLLA	1.4	560	360	-	-
Suuronen (1992)[6]	SR-PLLA	Screw*	-	200	7	110
Tormala (1992)[7]	SR-PLLA	1.3	-	300	10	220
Pohjonen (1997)[8]	SR-PLLA	Screw*	789	244	-	147

*The maximum thread diameter of the screw is 4.5 mm and the core diameter is 3.2 mm

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