

PREPARATION AND PROPERTIES OF HIGH STRENGTH RODS FROM *L*- AND *D,L*-LACTIDE COPOLYMER

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Abstract Starting with the *L*- and *D,L*-lactide copolymer (*L:DL* = 9:1) [P(*L-DL*)LA] of $M_w = 32.1 \times 10^4$, rods were obtained through a two stage process: (1) melt-extrusion at 155 °C, and (2) hot-drawing at 90 °C to various drawing ratios. The molecular weight of P(*L-DL*)LA fell to 9.3×10^4 as a consequence of the production process. The crystallization and molecular orientation of P(*L-DL*)LA developed as a result of the hot-drawing. The mechanical strengths of the rods increase with the drawing ratio. The maximum for tensile strength, bending strength, bending modulus, and shear strength are 329 MPa, 237 MPa, 8.8 GPa, and 157 MPa, respectively.

Keywords P(*L-DL*)LA, Self-reinforcement, Rod, Process, Bone fracture fixation

INTRODUCTION

Because of its biocompatibility and strong mechanical strength, PLLA (poly-*L*-lactide) has been widely studied for biomedical applications, such as drug delivery supports, body absorbable sutures, and bone fracture fixation devices^[1-3]. 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^[4, 5]. To avoid this negative side effect of PLLA, P(*L-DL*)LA having a low crystallinity is preferred. Another advantage of P(*L-DL*)LA is that it has a lower melting point than that of PLLA which means that P(*L-DL*)LA can be processed under relatively low temperatures so as to reduce the degree of thermal degradation during processing. 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 paper, the thermal transitions of P(*L-DL*)LA was discussed and the mechanical properties of the self-reinforced P(*L-DL*)LA [SR-P(*L-DL*)LA] rods were presented and compared with the SR-PLLA materials reported in literatures.

EXPERIMENTAL

Materials

PLLA and P(*L-DL*)LA were synthesized by ring opening polymerization in the bulk phase of lactides with stannous octoate as initiator^[6]. As the above literature mentioned, high molecular weight P(*L-DL*)LA would be obtained under the following reaction conditions: the high purity of monomer; the proper reaction temperature; the proper proportion of monomer with initiator and high vacuum. The polymerization products were purified by precipitation into methanol from the chloroform solution. The M_w of the resultant PLLA and P(*L-DL*)LA was 30.7 and 32.1×10^4 , respectively. The specific optical rotation for PLLA is -157° and for P(*L-DL*)LA is -140°.

The solution-precipitated P(*L-DL*)LA was granulated before use. The P(*L-DL*)LA rods were melt-extruded

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at 155°C on Brabender PLE-330 (Germany). The screw of the extruder is 19 mm in diameter and its rotation speed is 30 r/min. The nozzle of the extruder is 2 mm in diameter. The self-reinforcement was carried out by drawing the as-extruded rod to various drawing ratios ($\lambda = 2, 5$, and 7) at 90°C. The drawing ratio was defined as $\lambda = L/L_0$, where L_0 and L were the initial and final lengths of sheets before and after the drawing.

Measurements and Characterizations

The M_w of the polylactides was determined by gel permeation chromatography (GPC). The analyzer consisted of a Waters 510 HPLC pump, a PL gel column with a column temperature of 30°C, and a Waters 410 differential refractometer. The molecular weight was calibrated with polystyrene standards. Chloroform was used for elution, and a flow rate of 0.8 mL/min was applied.

Optical rotations of the polylactides were measured at room temperature in chloroform at a concentration of 0.2 g/dL on a WWZ-1 polarimeter (Physical Instruments, China).

The glass transition (T_g) and melting temperatures (T_m) and the enthalpies of crystallization (ΔH_c) and fusion (ΔH_m) were determined with a Netzsch DSC 204 differential scanning calorimeter calibrated with pure indium. T_m was taken as the maximum of the melting peak. The scan rate was 10 K/min in all cases, and the sample weight was between 5 and 7 mg. The crystallinity of the polylactides was evaluated according to the following equation:

$$\text{Crystallinity} = \frac{\Delta H_c + \Delta H_m}{\Delta H_m^0}$$

where ΔH_m^0 is the melting enthalpy of the 100% crystalline PLLA (93.0 J/g)^[7].

X-ray diffraction powder patterns were recorded with a Rigaku D/Max-2500 X-ray diffractometer using the $\text{CuK}\alpha$ radiation.

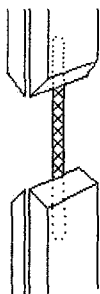


Fig. 1 The testing arrangements for the tensile test of P(L-DL)LA rods

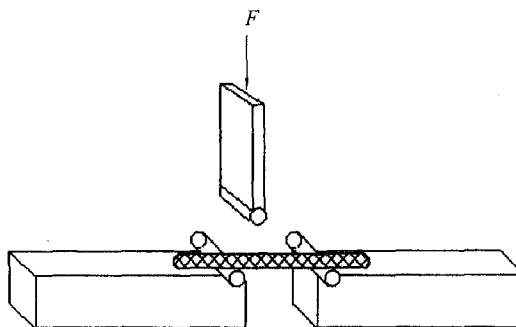


Fig. 2 The testing arrangements for the bending test of P(L-DL)LA rods

The mechanical strengths of P(L-DL)LA rods, including tensile strength, bending strength, bending modulus, and shear strength, were measured at room temperature with a Testometric Universal Tester M500-25 kN (England). The tensile strength was measured using the arrangement shown in Fig. 1. Both ends of the rod were fixed to the jaws of the tester and pulled out at a speed of 20 mm/min. To ensure that the pressing force of the jaws affixed to the ends of the rod is well distributed, the ends were bound with rubberized fabric. In most cases the tensile failure occurred at the center of the rods. In some cases the ends of the rod was broken. Only those test results in which the fractures occurred approximately in the center of the rods were calculated. The tensile strength was calculated by the following equation:

$$\sigma_t = \frac{4F_{\max}}{\pi d^2}$$

where σ_t = tensile strength (MPa), F_{max} = maximum pulling force (N), and d = diameter of the rod (mm).

The bending strength of P(L-DL)LA rods was measured by the three-point bending method (Fig. 2). The support span was 38 mm and the testing speed was 10 mm/min. The bending strength was calculated according to the equation:

$$\sigma_b = \frac{8F_{max}L}{\pi d^3}$$

where σ_b = bending strength (MPa), F_{max} = maximum bending force (N), L = support span (mm), and d = diameter of the rod (mm). The bending modulus was calculated by the equation (Fig. 3):

$$E_b = \frac{\Delta FL^3}{12\pi r^4 \delta}$$

where E_b = bending modulus (MPa), ΔF = bending force at the deformation δ (N), and r = radius of the rod (mm).

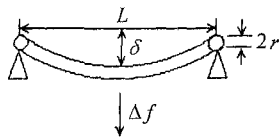


Fig. 3 Diagram illustrating the calculation of the bending modulus

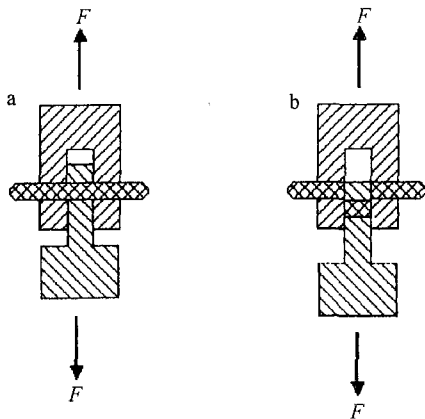


Fig. 4 The testing arrangements for the shear strength of P(L-DL)LA rods

The shear strength measurement of the P(L-DL)LA rods was conducted as shown in Fig. 4. The tool consisted of two parts that were joined together by the implant (Fig. 4a). The parts were pulled apart during the test using the Testometric Universal Tester M500-25 kN at a test speed of 20 mm/min, so that the rod resting in the drillhole was cut into pieces perpendicular to the long axis of the rod (Fig. 4b). The shear strength was calculated using the following equation:

$$\sigma_s = \frac{2F_{max}}{\pi d^2}$$

where σ_s = shear strength (MPa), F_{max} = maximum force recorded (N), and d = diameter of the rod (mm).

RESULTS AND DISCUSSION

Thermal Analysis

Depending on the manufacturing method of the P(L-DL)LA rods, they show different thermal transitions, as reported in the DSC thermograms of Fig. 5, and summarized in Table 1. The scan of the undrawn sheet shows a glass transition at 60.0°C, and a small melting peak at 151°C. But its crystallization exotherm is so irregular that it can not be easily recognized. In the absence of molecular orientation during the extrusion, the crystallization kinetics of PLLA is so slow that the polymer is easily quenched to a non-crystalline, amorphous state. The DSC curves of the SR-P(L-DL)LA sheets ($\lambda = 2, 5$, and 7) show a range of glass transition between 61.0°C and 69.1°C, a cold crystallization exothermic peak at 80–100°C, and a melting peak around 146°C. With increasing drawing ratio, the cold crystallization exothermic peak decreases, and the area of melting endotherm becomes bigger, resulting in the increase of the crystallinity. The increase of the degree of crystallization observed in our experiment may be due to the so-called stress-induced crystallization effect.

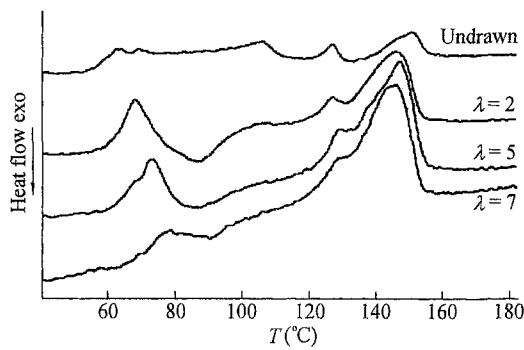


Fig. 5 DSC thermograms of P(L-DL)LA rods extruded at 155°C and drawn at 90°C to various drawing ratios

Table 1. DSC analysis of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios					
Manufacturing method ^a	T_g (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	Crystallinity (%)
Undrawn ^b	60.0	151	–	8.6	–
Orientation ($\lambda = 2$)	61.0	146	–4.4	25.2	22.4
Orientation ($\lambda = 5$)	62.1	147	–1.1	28.8	29.1
Orientation ($\lambda = 7$)	69.1	146	0	29.3	31.5

^a The orientation occurs under directional mechanical stress at 90°C and is fixed by quenching to room temperature.

^b $M_w = 9.3 \times 10^4$

By careful examination of the DSC thermograms in Fig. 5, two different melting peaks can be distinguished, at about 127 and 186°C, respectively. This double melting phenomenon may be caused by the presence of two distinct crystal structures or morphological structures in the P(L-DL)LA rods: (1) those existing before heating in the DSC instrument, and (2) those formed during the heating in the DSC instrument. We assume that the first peak (127°C) is related to the crystallization developed during the DSC scan, and the second one belongs to the crystal structure present in the initial sample. In order to determine whether this preliminary assessment is valid or not the melting curves of SR-P(L-DL)LA ($\lambda = 2$) were recorded at 10, 30 and 50 K/min (Fig. 6). When the scan rate is increased from 10 to 30 K/min, the intensity of the second peak increases with respect to the first peak, and it is also shifted to higher temperature by a few degrees. Finally, at 50 K/min, the first peak nearly vanishes with respect to the second peak and appears as a shoulder. These results provide a positive evidence for the assumption described above. When the heating rate is low, i.e., 10 K/min, there is enough time for the

molecular chain to crystallize and then melt. On the contrary, when the heating rate is high, i.e., 50 K/min, the crystallization step can hardly occur and the low temperature peak is hardly visible. The shift of the endotherms to higher temperatures may be related to the delay of the system to respond at high scanning rates.

Wide-Angle X-ray Scattering

Figure 7 depicts the X-ray diffraction curves of the solution-precipitated PLLA, SR-P(L-DL)LA rod ($\lambda = 7$) and P(L-DL)LA rod (undrawn). The undrawn rod has only merely amorphous scattering because of the absence of orientation. PLLA shows its most intense peak at 2θ values of 14.6, 16.5, 18.9 and 22.2°, which are in agreement with the peaks reported by Sarasua *et al.*^[8]. As for SR-P(L-DL)AL rod ($\lambda = 7$), only one main peak is observed at 2θ 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 2θ values of 14.6, 18.9 and 22.2° can not be detected.

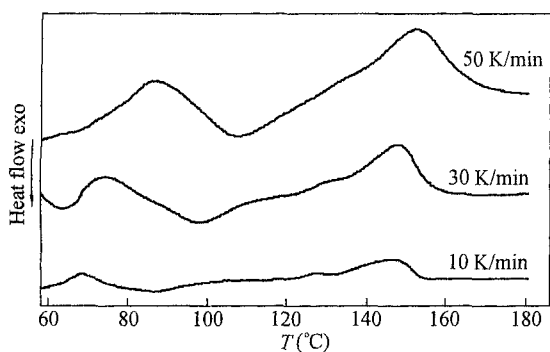


Fig. 6 DSC thermograms of the P(L-DL)LA rod ($\lambda=2$) heated at rates of 10, 30 and 50 K/min

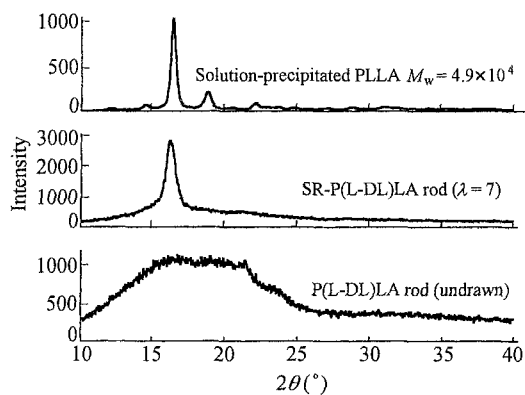


Fig. 7 X-ray diffraction curves of PLLA, SR-P(L-DL)LA rod ($\lambda = 7$) and P(L-DL)LA rod (undrawn)

To verify our assumption, the X-ray diffraction rocking curve of SR-P(L-DL)LA rod ($\lambda = 7$) was recorded. If there is no preferred orientation, i.e., crystallites at different angles with the sample surface are evenly distributed, the rocking curve should be a level line. In Fig. 8 the curve is approximately a normal distribution, and its maximum intensity is at the incident angle θ equal to 8.2°. This result strongly proves the existence of preferred orientation of crystallites in the direction parallel to the orientation axis of the rod.

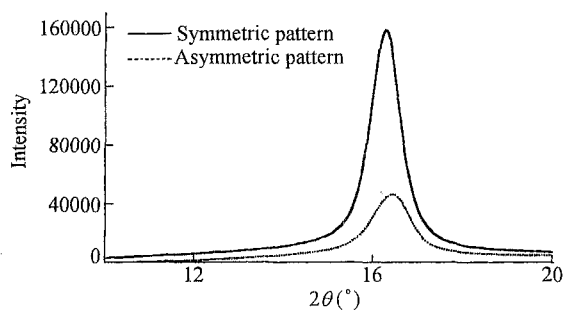


Fig. 8 Symmetric and asymmetric (declination angle = 5°) X-ray diffraction patterns of P(L-DL)LA sheet ($\lambda = 7$)

Mechanical Properties

Table 2 illustrates the mechanical properties of P(L-DL)LA rods extruded at 155°C and drawn at 90°C 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. Tensile strength changes from 59.9 to 329 MPa, bending strength from 147 to 237 MPa, and bending modulus from 2.8 to 8.8 GPa. These increments are the direct consequences of both crystallization development and preferred orientation of crystallites.

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 ($\lambda = 2$)	1.8	77.8	1.0	147	4.0	146
Orientation ($\lambda = 5$)	1.4	233	1.5	165	4.7	162
Orientation ($\lambda = 7$)	1.2	329	1.6	237	8.8	157

^a The orientation occurs under directional mechanical stress at 90 °C and is fixed by quenching to room temperature.

^b $M_w = 9.3 \times 10^4$

^c Test speed = 20.00 mm/min, sample length = 25.0 mm, sample type: circular

^d Test speed = 10.00 mm/min, support span: 38 mm

^e Test speed = 10.00 mm/min

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 merely measures the shear effect in the direction perpendicular to the orientation axis of the rod.

The mechanical strength data of SR-PLLA reported in the literatures are given in Table 3. From these comparative results it seems that SR-P(L-DL)LA is probably a suitable candidate for the fixation of bone fractures in terms of mechanical properties.

Table 3 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)
Present work	SR-P(L-DL)LA	1.2	329	237	8.8	157
Tormala (1990) ^[9]	SR-PLLA	1.4	560	360	—	—
Suuronen (1992) ^[10]	SR-PLLA	Screw *	—	200	7	110
Tormala (1992) ^[11]	SR-PLLA	1.3	—	300	10	220
Pohjonen (1997) ^[12]	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.

CONCLUSION

High strength P(L-DL)LA rods were produced by a combination of melt extrusion and self-reinforcement process. Depending on the drawing ratio of the rods, crystallization and preferred orientation of crystallites develop, with significant effects on the material’s mechanical properties. For SR-P(L-DL)LA rods the optimal values for tensile strength, bending strength, bending modulus, and shear strength are 329 MPa, 237 MPa, 8.8 GPa, and 157 MPa, respectively. These values are quite favorable for the application in the bone fracture fixation.

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