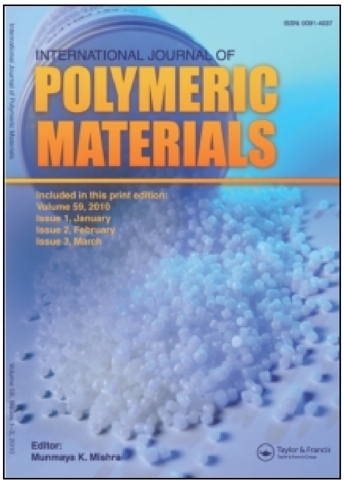

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Hu, Yushan , Zhang, Zhengpu , Song, Dong , Wang, Yongmei and Bai, Dongren(2002) 'Preparation and properties of high strength sheets from L- and D,L-lactide copolymer', International Journal of Polymeric Materials, 51: 12, 1071 — 1079

To link to this Article: DOI: 10.1080/714975699

URL: http://dx.doi.org/10.1080/714975699

International Journal of Polymeric Materials, 51:1071 – 1079, 2002
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0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290109859

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

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The solution-precipitated L- and D,L-lactide copolymer (L : D, L = 9 : 1) [P(L-DL)LA] showed a glass transition at 61.9°C, a melting peak at 153°C, and a crystallinity of 29.2%. After the extrusion and self-reinforcement, high strength sheets were achieved, with the maximum tensile strength and elastic modulus equal to 359 MPa and 7.0 GPa, respectively. It was found that self-reinforced P(L-DL)LA [SR-P(L-DL)LA] was strong enough in terms of tensile properties compared with self-reinforced poly(L-lactide) (SR-PLLA).

Keywords: polylactide, self-reinforcement, sheet, biomaterial

INTRODUCTION

PLLA, obtained by ring opening polymerization of L-lactide, is a biodegradable polyester. Because it degrades to nontoxic lactic acid, which is naturally present in the human body as a result of metabolism, PLLA and its copolymer have found uses in temporary medical applications such as drug delivery implants, body absorbable sutures, and bone fractures fixation devices. It is generally known that PLLA shows better mechanical strength than poly(D,L-lactide) (PDLLA), because PLLA is semi-crystalline while PDLLA is amorphous. But even for PLLA with an extremely high molecular weight (M_v up to 1×10^6), its mechanical properties are still poor under the traditional compression-molding processing method [1]. Therefore, in the late 1970 s Tormala *et al.*, used the self-reinforcing (SR) technique to develop PLLA composites which can attain much higher strengths than the earlier implants [2, 3]. The initial elastic bending modulus of

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Received 18 July 2000; in final form 3 August 2000.

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SR-PLLA screw amounts to 7 GPa, bending strength 200 MPa, shear strength 110 MPa, and maximum torque 0.2 ~ 0.3 Nm [4].

However, PLLA is a highly crystalline polymer and the degradation rate in a biological environment is rather slow. Furthermore, the crystalline domains remaining after partial degradation of the implant material give rise to an inflammatory response of the surrounding tissue [5, 6]. For this reason, materials of low crystallinity are preferred in surgical applications. The crystallinity of the L-lactide homopolymer can be conveniently modified by the copolymerization of L-lactide with D,L-lactide. In our experiment, P(L-DL)LA was synthesized and high strength copolymer sheets were achieved after extrusion and self-reinforcement. In this article, the thermal transitions of P(L-DL)LA and the mechanical properties of the SR-P(L-DL)LA sheets are discussed. The structure of the SR-P(L-DL)LA sheets was studied by wide-angle X-ray scattering.

EXPERIMENTAL

Materials

PLLA, P(L-DL)LA, and PDLLA were synthesized in the bulk phase by ring opening polymerization of lactides with stannous octoate as initiator. The polymerization products were purified by precipitation into methanol from a chloroform solution. The weight-average molecular weight of the resultant PLLA, P(L-DL)LA, and PDLLA was 30.7, 32.1 and 17.6×10^4, 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 the process. The P(L-DL)LA sheets were melt-extruded at 175°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 exit of the extruder is 50 mm wide and 0.5 mm thick. The self-reinforcement was carried out by drawing the as-extruded sheet to various drawing ratios ($\lambda = 2$, 5 and 7) at 75°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 weight-average molecular weight of the polylactides was determined by gel permeation chromatography (GPC). The analyzer was composed 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 according to 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 Instrument Plant, Shanghai, P. R. China).

The glass transition and melting temperatures (T_g and T_m, respectively) and the enthalpies of crystallization and fusion (ΔH_c and ΔH_m, respectively) 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 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 Cu K_α radiation.

Tensile mechanical measurements were performed at room temperature with a Testometric Universal Tester M500-25 kN at a speed of 20 mm/min. The samples were cut into dumbbell specimens before tests as recommended in standard GB 1040-79. Fracture always occurred approximately in the center of the sheets.

RESULTS AND DISCUSSION

Properties of Solution-Precipitated P(L-DL)LA

Thermal Analysis

Figure 1 shows the thermal behavior of solution-precipitated polylactides having different optical purities. It is seen that PLLA gives a strong single endothermic peak at 177°C, while the melting peak of P(L-DL)LA appears near 153°C. The melting point depression of the P(L-DL)LA may be explained using Flory's equation for random copolymerization

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m^0} \ln X_L$$

where T_m is the melting temperature of the copolymer, T_m^0 the melting temperature of the parent homopolymer, R the gas constant, X_L the molar fraction of crystallizable L units, and ΔH_m^0 the enthalpy of fusion per molar repeating L units. Here, X_L is calculated from the enantiometric excess of the polymer which is taken equal to 0.9, the experimentally measured optical purity, T_m^0 is taken equal to 454 K [8], and $\Delta H_m^0 = 6.7$ kJ/mol (see previous

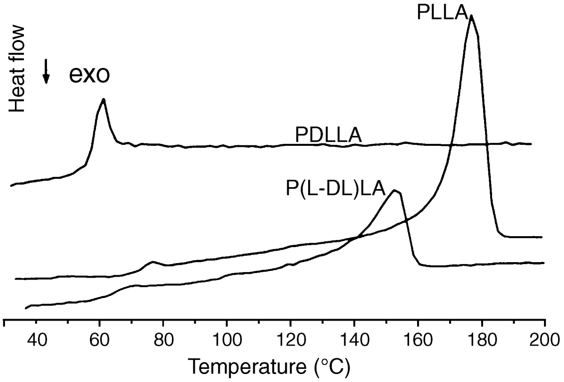

FIGURE 1 DSC thermograms of solution-precipitated polylactides having different optical purities.

section). The calculated value approximately equals the experimental value. 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. As for PDLLA, apart from a small endothermic peak directly above the glass transition area, no melting endotherm can be detected. This means that PDLLA is completely amorphous and non-crystallizable.

The glass transition temperatures, the enthalpies and temperatures of fusion, and the crystallinity of solution-precipitated polylactides with different optical purities are reported in Table 1. It is emphasized that the crystallinity of polylactides improves with the optical purity, and consequently, the glass transition temperature also increases.

Wide-Angle X-ray Scattering

Figure 2 gives the X-ray diffraction patterns of solution-precipitated PLLA, P(L-DL)LA, and PDLLA. PLLA shows its most intense peaks at 2θ values of 14.6, 16.5, 18.9 and 22.2°, in agreement with the peaks reported at 14.5, 16.3, 18.7 and 21.9° by Sarasua *et al.* [9] for the α-form of the optically pure

TABLE 1 DSC analysis of solution-precipitated polylactides having different optical purities

Sample	T_g (°*C*)	T_m (°*C*)	ΔH_c (*J*/*g*)	ΔH_m (*J*/*g*)	*Crystallinity* (%)
PLLA	72.3	177	–	48.9	52.5
P(L-DL)LA	61.9	153	–	27.2	29.2
PDLLA	56.9	–	–	–	–

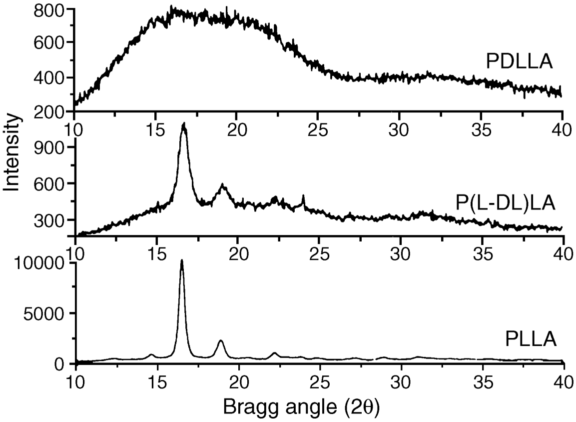

FIGURE 2 X-ray diffraction curves of solution-precipitated polylactides having different optical purities.

PLLA crystallizing in a pseudo-orthorhombic unit cell of dimensions $a = 1.07\,\text{nm}$, $b = 0.595\,\text{nm}$ and $c = 2.78\,\text{nm}$, which contains two 10_3 helices [10]. As expected, P(L-DL)LA exhibits a diffraction pattern that agrees closely with that of PLLA. PDLLA has only amorphous scattering because of the absence of crystallinity, corresponding to the conclusion drawn from the DSC analysis.

Properties of Extruded and Self-Reinforced P(L-DL)LA Sheets

Thermal Analysis

Depending on the manufacturing method of the P(L-DL)LA sheets, they have different thermal transitions, as shown in the DSC thermograms of Figure 3, and summarized in Table 2. The scan of the undrawn sheet shows a glass transition at 55.7°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 glass transition range between 60.7°C and 66.8°C, a cold crystallization exothermic peak at 85 ~ 105°C, and a melting peak around 151°C. With increasing drawing ratio, the cold crystallization exothermic peak decreases, and the area of melting endotherm becomes bigger, resulting in an increase of the crystallinity. The increase in the degree of crystallinity observed in our experiment may be due to the so-called stress-induced crystallization effect.

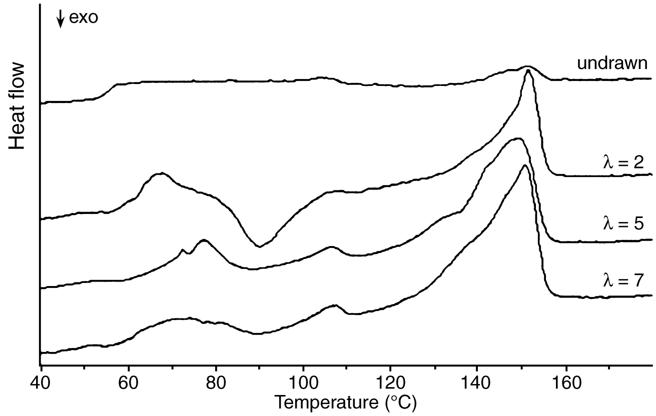

FIGURE 3 DSC thermograms of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios.

TABLE 2 DSC analysis of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios

*Manufacturing method**	T_g (°*C*)	T_m (°*C*)	ΔH_c (*J*/*g*)	ΔH_m (*J*/*g*)	*Crystallinity* (%)
undrawn**	55.7	151	–	5.0	–
orientation($\lambda = 2$)	60.7	152	– 13.9	23.8	10.6
orientation($\lambda = 5$)	62.5	151	– 2.9	26.6	25.5
orientation($\lambda = 7$)	66.8	149	– 1.4	27.2	27.7

* The orientation occurs under directional mechanical stress at 75°C and is fixed by quenching to room temperature.
** $M_w = 4.9 \times 10^4$.

Wide-Angle X-ray Scattering

Figure 4 gives the X-ray diffraction curves of P(L-DL)LA sheets (undrawn, $\lambda = 2$ and $\lambda = 7$). Clearly, the undrawn sample shows the amorphous scattering. As to SR-P(L-DL)LA sheets ($\lambda = 2$ and $\lambda = 7$), only one main peak is observed at 2θ of 16.5°. Comparing the X-ray diffraction curve of PLLA in Figure 2 and that of SR-P(L-DL)LA in Figure 4, 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.

To verify our hypothesis, the asymmetric (declination angle = 5°) X-ray diffraction patterns of P(L-DL)LA sheet ($\lambda = 7$) was recorded. As shown in Figure 5, when the sample sheet is turned by 5° taking the normal of sheet surface as axis, the intensity of the crystalline peak at 2θ value of 16.5° decreases markedly. This phenomenon qualitatively proves that a preferred

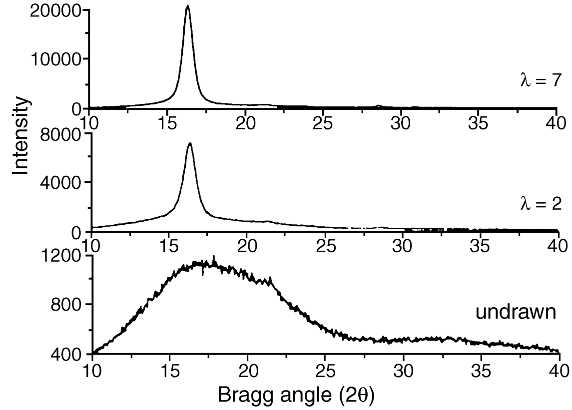

FIGURE 4 X-ray diffraction curves of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios.

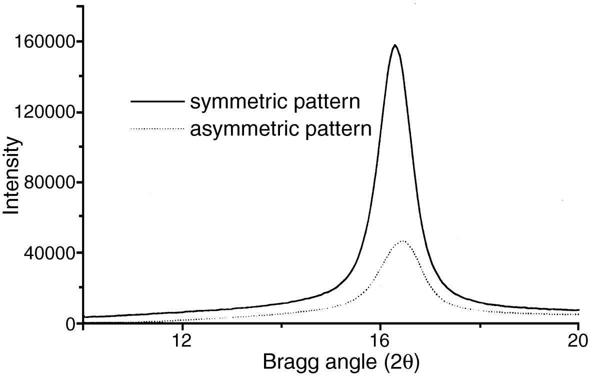

FIGURE 5 Symmetric and asymmetric (declination angle = 5°) X-ray diffraction patterns of P(L-DL)LA sheet ($\lambda = 7$).

orientation of crystallites does exist in a direction parallel to the orientation axis of the sheet.

Mechanical Properties

Figure 6 shows the stress–strain curves for the P(L-DL)LA sheets, as reported in Table 3. It can be clearly seen that the mechanical properties, including yield stress, tensile strength, and elastic modulus, improve significantly as the drawing ratio increases, as a direct consequence of both crystallization development and preferred orientation of crystallites. Yield

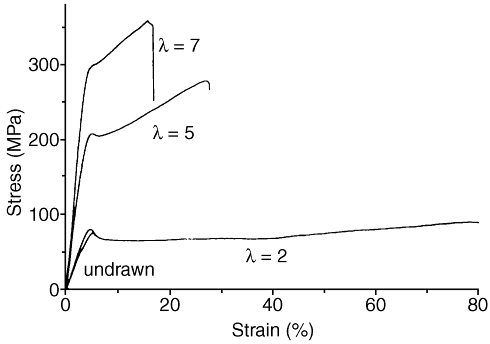

FIGURE 6 Stress–strain curves of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios.

TABLE 3 Stress–strain properties of P(L-DL)LA sheets extruded at 175°C and drawn to various drawing ratios*

*Manufacturing method***	*Sheet thickness (mm)*	*Yield stress (MPa)*	*Tensile strength (MPa)*	*Elastic modulus (GPa)*	*Elongation at yield (%)*	*Elongation at break (%)*
undrawn***	0.20	74.3	74.3	1.8	5.3	5.7
orientation($\lambda = 2$)	0.10	79.1	89.7	1.8	4.8	85.0
orientation($\lambda = 5$)	0.04	208	278	5.5	5.2	34.4
orientation($\lambda = 7$)	0.02	290	359	7.0	5.0	17.1

*The tensile tests are carried out according to GB 1040-79, and the test speed is 20 mm/min.

**The orientation occurs under directional mechanical stress at 75°C and is fixed by quenching to room temperature.

*** $M_w = 4.9 \times 10^4$.

stress changes from 74.3 to 290 MPa, tensile strength from 74.3 to 359 MPa, and elastic modulus from 1.8 to 7.0 GPa.

Taking elongation at yield and elongation at break into consideration, for the undrawn sheet, where there is no orientation and little crystallinity, the as-extruded sheet is relatively brittle and breaks (elongation at 5.7%) immediately after the yield point (elongation at 5.3%). This is apparently due to the glassy nature of the sheet. Introduction of some molecular orientation into the sheets does not bring much change to the elongation at yield, but causes a substantial increase in ductility (for $\lambda = 2$, 5 and 7, elongation at break is 85.0, 34.4 and 17.1%, respectively).

CONCLUSION

P(L-DL)LA is a crystallizable polymer exhibiting a glass transition at 61.9°C, a melting peak at 153°C, and crystallinity of 29.2% under the solution-precipitation condition. It possesses the α-form of the optically pure PLLA crystallizing in a pseudo-orthorhombic unit cell of dimensions $a = 1.07\,\mathrm{nm}$, $b = 0.595\,\mathrm{nm}$ and $c = 2.78\,\mathrm{nm}$, which contains two 10_3 helices. The self-reinforcing technique induces crystallization and a preferred orientation of crystallites, resulting in an increase of yield stress, tensile strength, elastic modulus, and ductility. The maximum tensile strength and elastic modulus observed in the present study are 359 MPa and 7.0 GPa, respectively. These values are quite sufficient compared to those of the SR-PLLA reported by Tormala *et al.* [2]. Other mechanical properties of the SR-P(L-DL)LA, such as bending strength, bending modulus, and shear strength, will be reported later.

REFERENCES

[1] Leenslag, J. W., Pennings, A. J., Bos, R. R. M., Rozema, F. R. and Boering, G. (1987). *Biomaterials*, **8**, 70.

[2] Tormala, P., Rokkanen, P., Vainionpaa, S., Laibo, J., Heponen, V.-P. and Pohjonen, T. (1990). *US. Patent 4,968,317.*

[3] Tormala, P. (1992). *Clin. Mater.*, **10**, 29.

[4] Suuronen, R., Pohjonen, T., Taurio, R., Tormala, P., Wessman, L., Ronkko, K. and Vainionpaa, S. (1992). *J. Mater. Sci.: Mater. Med.*, **3**, 426.

[5] Penning, J. P., Grijpma, D. W. and Pennings, A. J. (1993). *J. Mater. Sci. Lett.*, **12**(13), 1048.

[6] Tams, J., Joziasse, C. A. P., Bos, R. R. M., Rozema, F. R., Grijpma, D. W. and Pennings, A. J. (1995). *Biomaterials*, **16**, 1409.

[7] Shinno, K., Miyamoto, M. and Kimura, Y. (1997). *Macromolecules*, **30**, 6438.

[8] Jamshidi, K., Hyon, S.-H. and Ikada, Y. (1988). *Polymer*, **29**, 2229.

[9] Sarasua, J.-R., Prud'homme, R. E., Wisniewski, M., Borgne, A. L. and Spassky, N. (1998). *Macromolecules*, **31**, 3895.

[10] Okihara, T., Tsuji, M., Kawaguchi, A. and Katayama, K.-I. (1991). *J. Macromol. Sci. – Phys.*, **B30**(1 and 2), 119.