

# Effect of Molecular Weight and Crystallinity on Poly(lactic acid) Mechanical Properties

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## SYNOPSIS

Several samples of poly(lactic acid) with different molecular weights and tacticity have been prepared, and some PLLA injection moulded specimens have been annealed to promote their crystallization. From the characterization data, poly(L-lactide) showed more interesting mechanical properties than poly(D,L-lactide), and its behavior significantly improves with crystallization. In fact, annealed specimens possess higher values of tensional and flexural modulus of elasticity, Izod impact strength, and heat resistance. The plateau region of flexural strength as a function of molecular weights appears around  $M_v = 35,000$  for PDLLA and amorphous PLLA and at higher molecular weight, around  $M_v = 55,000$ , for crystalline PLLA. The study of temperature effect shows that at 56°C only crystalline PLLA still exhibits useful mechanical properties. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Scientific and industrial interest in lactic acid polymers is increasing, not only for biomedical applications, but also for potential large-scale uses, such as packaging and many consumer goods.<sup>1</sup> In spite of the very good thermoplastic behavior of these materials, the relatively high cost of the intermediate lactide deeply affects the possibility of their commercialization<sup>2-4</sup>: an intensive purification, based on several crystallizations, is in fact generally required for reaching high-molecular-weight polymers and, consequently, useful mechanical properties. In this context, the industrial manufacturing of lactic acid polymers for high volume production should be oriented by evaluating the correlations between molecular weight and characteristics of the material. Moreover, lactic acid crude polymers easily show a thermal degradation during melt processing,<sup>5-7</sup> with relevant reduction of molecular weight. This also affects the properties of these materials with unfavorable consequences in several application fields.

The aim of this research was to investigate the

correlation between molecular weight of poly(L-lactide) (PLLA) and poly(D,L-lactide) (PDLLA) and their mechanical properties. We decided to characterize medium- and low-molecular-weight samples since they can be obtained from monomers having received less purification steps and because they can derive from the degradation of higher molecular weight materials.

The polymers were synthesized by ring opening polymerization of L- and D,L-lactide with Sn(II) 2-ethylhexanoate (stannous octoate), as described in a previous paper<sup>8</sup> and generally in the chemical literature.<sup>9-11</sup>

We decided to prepare lower molecular weight samples by extruding the polymers several times without any purification or stabilization step. It is well known that in these conditions lactic acid polymers exhibit a fast degradation,<sup>5,6</sup> especially if it is associated with hydrolytic phenomena.

Besides mechanical testing the injection moulded specimens as obtained, we annealed some PLLA samples to induce their crystallization and to study the effect on the material behavior. Especially in the case of amorphous PDLLA, the relatively low glass transition temperature ( $T_g$ ) can affect the performances of the shaped objects during applications or even after storage. It was then of relevant interest to investigate the effect of temperature on poly(lactic acid) mechanical behavior.

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## EXPERIMENTAL

### Materials

L- and D,L-Lactic acid (Fluka) were used as received at a concentration of 90%; methyl isobutyl ketone (Rudipont) was dried on activated 3A molecular sieves.

The preparation of L- and D,L-lactide has been described in detail previously.<sup>5</sup> Briefly, 90% lactic acid was oligomerized at 200°C and thermally converted to lactide by tin powder catalysis. The product, vacuum distilled, was purified by several crystallizations with methyl isobutyl ketone up to a melting point of 94–96°C for L-lactide and 124–126°C for D,L-lactide. The purified L-lactide showed  $[\alpha]_D^{25} = -263^\circ$  in methylene chloride. Sn(II) 2-ethylhexanoate (Sigma) was kept under nitrogen, on activated 3A molecular sieves, and used as a polymerization catalyst.

### Synthesis

The polymerizations were carried out under nitrogen in two neck 1000-mL glass flasks, in which 800 g of lactide was introduced. Each flask was immersed in an oil bath thermostated at 130°C and, after the melting of monomer, 0.450 g of pure Sn(II) 2-ethylhexanoate was added; this amount corresponds to a monomer/initiator molar ratio of 5000/1. Magnetic stirring, possible during the first hour of reaction, made the system homogeneous. After a polymerization time of 24 h, the polymers were recovered and characterized in terms of viscosity, ranging from 3.30 to 4.88 dL/g for PLLA and from 3.18 to 3.40 for PDLA.

### Preparation of Samples

The crude polymers were cut in small pieces, then grinded to get granules with size range of 2–4 mm. For degradation an extruder Haake Rheocord EC was employed with four heating zones, air cooling, and screw speed of 32 rpm. The temperature profile of the four heating zones was 180, 180, 195, and 190°C (head) for poly(L-lactide) and 120, 140, 140, and 130°C (head) for poly(D,L-lactide).

The dumbbell specimens for mechanical testing were obtained by injection moulding the materials in a Sandretto series 60 press at a temperature of 195°C for PLLA and 140°C for PDLA. Injection moulding was accompanied by an additional decrease of molecular weight ranging from 14 to 40%; the characteristics of the materials after processing are reported in Table I.

### Characterization

The inherent viscosities of the materials were measured in chloroform at 25°C at a concentration of 0.20 g/dL, and are expressed in dL/g. The viscosity data were converted into molecular weights with the Mark-Houwink equation in the following forms<sup>12</sup>:

$$\text{PLLA: } \eta = 5.45 \times 10^{-4} \bar{M}_v^{0.73}$$

$$\text{PDLA: } \eta = 2.21 \times 10^{-4} \bar{M}_v^{0.77}$$

Thermal parameters were determined by differential thermal calorimetry (Perkin Elmer DSC 7, calibrated with an indium standard) with a heating rate of 10°C/min. The melting enthalpies of the specimens were calculated as a difference between

**Table I** Physicochemical Data of the Specimens Tested

Sample	Viscosity (dL/g)	$\bar{M}_v$	$T_g$ (°C)	$T_m$ (°C)	$\Delta H$ (J/g)	$[\alpha]_D^{25}$ (°)
PLLA I	0.83	23,000	59	178	8	-157
PLLA II	1.04	31,000	55	178	13	-159
PLLA III	1.64	58,000	58	179	8	-159
PLLA IV	1.80	66,000	59	181	3	-160
Ann. PLLA I	0.74	20,000	59	178	65	-158
Ann. PLLA II	1.02	30,000	59	178	59	-157
Ann. PLLA III	1.41	47,000	59	180	48	-158
Ann. PLLA IV	1.80	66,000	61	178	42	-160
PDLA I	0.88	47,500	52	—	—	—
PDLA II	1.25	75,000	50	—	—	—
PDLA III	1.73	114,000	49	—	—	—

the hexothermic heat of melting and the endothermic crystallization heat: this was necessary to eliminate the contribution of crystallinity produced during the test.

Optical rotations were measured at 25°C on a Perkin Elmer polarimeter 241, in a 6 mL cell with a length of 10 cm, at the D line of sodium ( $\lambda = 589$  nm). A concentration of 0.8 g/100 mL was used in all cases and the values are expressed as  $[\alpha]_D^{25}$ .

The mechanical characterization was performed on specimens maintained in anhydrous conditions. We measured tensile properties according to ASTM D-638, with dumbbells type I, 3 mm thick, at a speed of 50 mm/min. For the flexural measures, small bars,  $80 \times 12 \times 3$  mm, were used according to ASTM D-790, method 1, procedure A, at 1.25 mm/min. Tensile and flexural testing were carried out at 23°C, relative humidity of 55%, with an Instron dynamometer, 4502. The same bars for flexural testing were used for Izod impact test, at 23°C, according to ASTM D-256, methods A and E.

For heat distortion testing, small bars,  $120 \times 13 \times 3$  mm, were employed, by applying a strength of 1820 kPa, and adopting ASTM D-648. The data were obtained with a CEAST HDT/Vicat 6505. For the Vicat test, specimens of  $19 \times 40 \times 3$  mm were loaded with 1000 g according to ASTM D-1525. The measures of Rockwell hardness were obtained according to ASTM D-785, procedure A, with specimens of  $30 \times 19 \times 3$  mm. The experimental conditions were 10 kg of preloading, 60 kg of loading, drift of  $\frac{1}{8}$  in., and loading time of 15 s.

## RESULTS AND DISCUSSION

The crystallization of PLLA has been described in the chemical literature by several authors,<sup>12-14</sup> but less known is the effect of crystallization on the mechanical properties of this material. By injection molding poly(L-lactide), the manufactured articles are generally amorphous, because of the slow crystallization kinetic of this polymer. Actually, the PLLA samples that are described as "amorphous" in the present paper show a crystallinity of about 3–13 J/g, which is very low if compared to the heat of fusion of highly crystalline poly(L-lactide), which is generally of 76–78 J/g.<sup>15</sup>

Only at suitable conditions, such as a very slow cooling or by adding a nucleating agent, can the samples become really crystalline. A specific treatment being necessary to improve the crystallinity, we wanted to understand how much this parameter affects the behavior of poly(L-lactic acid) and, more

generally, our aim was to obtain a comparison with poly(D,L-lactic acid), which is, as known, completely amorphous.

The determination of PLLA crystallization kinetics is already available in the chemical literature<sup>10,14</sup> and, according to the published results, our preliminary tests showed that an effective treatment to get crystallinity is the annealing of the specimens at 105°C for 90 min under nitrogen, therefore this was the chosen method.

After this treatment, the materials showed a crystallinity of 42–65 J/g, as determined by DSC analysis, depending on the molecular weight ( $\bar{M}_v$ ). From the experimental data it appears in fact that lower molecular weights allowed, at equal conditions, a more complete crystallization, due to increased chain mobility.<sup>16</sup>

The physicochemical properties of the tested specimens are shown in Table I, from which there does not appear to be any dependence of  $T_g$  from the molecular weights ( $\bar{M}_v$ ) of the examined samples, ranging from 20,000 to 66,000 for PLLA and from 47,500 to 114,000 for PDLLA (Table I). In the group of the explored materials, the melting temperatures do not show any significant correlation with molecular weights, which seem to influence, as reported above, only the extent of crystallinity.

The method employed to prepare lower molecular weight samples was based on several extrusions, that are a possible cause of racemization and consequently of a reduced crystallizability, so the optical activity of PLLA specimens was checked as a function of extrusion cycles. A very small variation of optical activity (2–3°), near the experimental error, is observed from the data reported in Table I, therefore it is possible to observe that basically the material maintained its chirality.

From the analysis of mechanical data reported in Tables II and IV we see that, in the above mentioned range of molecular weights, PDLLA and amorphous PLLA present a small change of tensile properties: the strength (stress at break) is characterized for PLLA by values ranging from 55 to 59 MPa, and in the case of PDLLA by values included between 40 and 44 MPa. However, amorphous PLLA shows a better behavior, if we consider that a tensile strength of 59 MPa is associated with  $\bar{M}_v = 67,000$ , while PDLLA with  $\bar{M}_v = 114,000$  shows a tensile strength of 44 MPa. This can be due to the stereoregularity of the polymer chain, which in the case of PLLA is characterized by the presence of only S(–) chiral centers.

It is interesting to note that annealed PLLA, whose mechanical properties are reported in Table

**Table II Mechanical Properties of Poly(L-lactide) Specimens as Obtained**

Sample	PLLA I	PLLA II	PLLA III	PLLA IV
$\bar{M}_v$	23,000	31,000	58,000	67,000
Tensile properties				
Yield strength (MPa)	—	65	68	70
Tensile strength (MPa)	59	55	58	59
Yield elongation (%)	—	2.2	2.3	2.2
Elongation at break (%)	1.5	5.5	5.0	7.0
Modulus of elasticity (MPa)	3550	3550	3750	3750
Flexural properties				
Flexural strength (MPa)	64	97	100	106
Maximum strain (%)	2.0	4.2	4.1	4.7
Modulus of elasticity (MPa)	3650	3600	3600	3650
Impact resistance				
Notched strength (J/m)	19	22	25	26
Unnotched strength (J/m)	135	175	185	195
Heat resistance				
HDT (°C)	57	55	—	55
Vicat penetration (°C)	60	59	59	59
Hardness				
Rockwell hardness (HR)	85	84	83	88

III, shows a clearer variation, by changing the tensile strength from 47 to 66 MPa in the same range of molecular weights. Evidently, the crystalline fraction of this material is more influenced by this increment of molecular weights, despite the moderate reduction of crystallinity extent, from 65 to 42 J/g, associated with the same increment.

As expected, annealed PLLA samples present the highest tensile modulus of elasticity, with values ranging from 4000 to 4200 MPa, compared with 3550–3750 MPa characterizing PLLA nonannealed samples.

The flexural strength changes from 84 to 88 MPa for PDLA, and from 64 to 106 MPa for amorphous

**Table III Mechanical Properties of the Annealed Poly(L-Lactide) Specimens**

Sample	Ann. PLLA I	Ann. PLLA II	Ann. PLLA III	Ann. PLLA IV
$\bar{M}_v$	20,000	33,500	47,000	71,000
Tensile properties				
Yield strength (MPa)	—	63	68	70
Tensile strength (MPa)	47	54	59	66
Yield elongation (%)	—	1.8	2.2	2.0
Elongation at break (%)	1.3	3.3	3.5	4.0
Modulus of elasticity (MPa)	4100	4100	4050	4150
Flexural properties				
Flexural strength (MPa)	51	83	113	119
Maximum strain (%)	1.6	2.3	4.8	4.6
Modulus of elasticity (MPa)	4200	4000	4150	4150
Impact resistance				
Notched strength (J/m)	32	55	70	66
Unnotched strength (J/m)	180	360	340	350
Heat resistance				
HDT (°C)	66	60	—	61
Vicat penetration (°C)	157	159	163	165
Hardness				
Rockwell hardness (HR)	84	82	84	88

**Table IV Mechanical Properties of Poly(D,L-lactide) Specimens**

Sample	PDLLA I	PDLLA II	PDLLA III
$\bar{M}_v$	47,500	75,000	114,000
Tensile properties			
Yield strength (MPa)	49	53	53
Tensile strength (MPa)	40	44	44
Yield elongation (%)	1.7	1.4	1.5
Elongation at break (%)	7.5	4.8	5.4
Modulus of elasticity (MPa)	3650	4050	3900
Flexural properties			
Flexural strength (MPa)	84	86	88
Maximum strain (%)	4.8	4.1	4.2
Modulus of elasticity (MPa)	3500	3550	3600
Impact resistance			
Notched strength (J/m)	18	17	18
Unnotched strength (J/m)	135	140	150
Heat resistance			
HDT (°C)	51	50	50
Vicat penetration (°C)	52	53	52
Hardness			
Rockwell hardness (HR)	78	72	76

PLLA. In the case of crystalline PLLA the same parameter increases from 51 to 119 MPa, at increasing molecular weights.

The influence of molecular weight on flexural strength from the trends of amorphous and annealed PLLA is based on the fact that both tensile and flexural properties increase with the crystallization degree, as discussed above. In particular, amorphous PLLA seems to reach a plateau around  $\bar{M}_v = 35,000$ , while for crystalline PLLA the same behavior is obtained at higher molecular weights, around  $\bar{M}_v = 55,000$ , but also with higher tensile and flexural strength.

As expected, the impact resistance measures have given more regular data of notched than unnotched strength, with values of notched strength ranging from 19 to 26 J/m for amorphous PLLA, from 32 to 66–70 J/m for annealed PLLA, and about 18 J/m for PDLLA. The progressive increment of impact strength of PLLA samples indicates that, in the investigated range of molecular weights, this parameter is still increasing, mainly for crystalline specimens. These samples exhibit, in fact, a variation around 100%, compared to a 37% change for PDLLA specimens: evidently the effect of the molecular weight increment on impact resistance is amplified by the crystallization of the material.<sup>17</sup> As confirmation, PDLLA samples showed no variation of impact strength with the molecular weight, due to their complete amorphous nature. This material also

presents the lowest values, showing that crystalline or partially crystalline PLLA is more suitable than PDLLA for applications that require a high impact resistance.

While we did not observe a well-defined correlation between heat resistance and molecular weights among the samples studied, the data reported reveal different HDT for the three groups of materials. PDLLA showed the lowest heat resistance, which is around 50°C, while for amorphous and crystalline PLLA, the HDT values are 55–57 and 60–66°C, respectively. The different heat resistances are easily understandable if we think about the physicochemical properties of these materials; in fact PDLLA exhibits the lowest  $T_g$ , of about 50°C, corresponding nearly to its HDT. Also in the case of amorphous PLLA there is a correspondence between measured  $T_g$  (55–59°C) and HDT, while crystalline PLLA is slightly influenced by its crystallinity and reaches higher heat resistances. As expected, Vicat penetration was much more influenced by crystallinity, so in the case of PDLLA and amorphous PLLA we measured values of 52–53 and 59–60°C, respectively, that is, also in this case, very near to their  $T_g$ , while crystalline PLLA presented a very different behavior, with values of 157–165°C.

The marked effect of crystallinity of poly(lactic acid) on its heat resistance induced us to characterize the flexural properties of these materials at higher temperatures and exactly at 36 and 56°C,

**Table V Influence of Temperature on Flexural Properties**

Sample	PDLLA II	PLLA III	PLLA III ann.
$\bar{M}_v$	75,000	58,000	47,000
$T_g$ (°C)	50	58	59
$\Delta H$ (J/g)	0	8	48
Properties at 23°C			
Flexural strength (MPa)	86	100	113
Max. strain (%)	4.1	4.1	4.8
Modulus of elasticity (MPa)	3550	3600	4150
Properties at 36°C			
Flexural strength (MPa)	60	77	83
Max. strain (%)	3.3	3.9	4.3
Modulus of elasticity (MPa)	2800	3400	3600
Properties at 56°C			
Flexural strength (MPa)	0.2	0.4	28
Max. strain (%)	n.r.	8	7.5
Modulus of elasticity (MPa)	25	50	950

that is remaining below their  $T_g$ . The results, reported in Table V, show that between 23 and 36°C, PDLLA is characterized by a reduction of flexural strength of 30%, while amorphous and crystalline PLLA show a change of 23 and 26%, respectively, of the same parameter. Much more dramatic are the variations determined at 56°C, where only crystalline PLLA reaches useful mechanical properties, even with a flexural strength (28 MPa) and a modulus of elasticity (950 MPa) that are only 25 and 23% of the values determined at 23°C. So the very small amount of crystallinity characterizing the PLLA samples that in the present paper we described as "amorphous" (3–13 J/g) does not appear sufficient to affect significantly their heat stability. The choice of an optically active poly(lactic acid) and an effective crystallization are necessary requisites, if the material is needed at temperatures of 50°C or higher.

Much less influenced by crystallinity seems to be the Rockwell hardness of these materials, which is nearly equal for amorphous and crystalline PLLA, with values of 83–88 and 82–88 HR, respectively. Also the dependence of Rockwell hardness from molecular weights seems vague, while the effect of  $T_g$  is more evident: PDLLA, in fact, shows a minor hardness, included between 72 and 78 HD.

## CONCLUSIONS

The mechanical characterization of poly(lactic acid) samples having different tacticity and molecular weights has evidenced relevant differences, which

can be useful for the choice of the proper materials for specific applications.

The characterization data have shown more interesting tensile and flexural properties for both amorphous and crystalline PLLA than in the case of PDLLA, probably due to the stereoregular nature of poly(L-lactic acid) chain. The increment of molecular weight has shown a marked effect mainly on the properties of crystalline PLLA, which seems to reach a plateau of property values at higher molecular weights, around  $\bar{M}_v = 55,000$ . Also the impact resistance is very influenced by crystallinity and, in the case of annealed PLLA, by the evaluated increment of molecular weight. While PDLLA and amorphous PLLA present a heat resistance very near to their  $T_g$ , annealed PLLA shows a better behavior: only this material can be used at a temperature of 50°C or higher, because its crystallinity stabilizes its properties.

In conclusion, the crystallization of these materials, possible only in the case of an optically active poly(L-lactic acid), significantly improves their mechanical behavior and it is an important condition for applications at temperatures of 40–50°C or higher.

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