

Crystallization and thermal behaviour of optically pure polylactides and their blends

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Lactic acid based polymers of medical grade were crystallized under isothermal and non-isothermal conditions from the melt. Optically pure enantiomeric polylactides, Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA), are found to crystallize as α crystalline form. PLLA/PDLA blends were prepared by a melt mixing process and during solidification yielded both lower melting α homocrystallites and higher melting stereocomplex crystallites. The effects of isothermal and non-isothermal crystallization conditions on developed polymorphism and degree of crystallinity are evaluated for PLLA/PDLA blends.

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1. Introduction

Poly lactides are candidate materials for temporary uses in medicine [1]. Being biodegradable and bioresorbable polylactides can be used in repair and regeneration of healing tissues. Polylactides also fulfil many requirements of packaging thermoplastics [2] and are being developed as commodity resins for general packaging applications [3, 4].

Lactic acid (2-hydroxypropanoic acid) is an optically active molecule that exists in both L (+) and D (–) stereoisomers. Polymerization of lactide by a ring opening polymerisation mechanism results in polylactide with lactyl structural units incorporated by pairs into the macromolecular backbone [5]. Fig. 1 shows the stereoisomers of optically pure polylactides. Both polylactides, Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA), are prepared by incorporating respectively 100% L-units or 100% D-units, while racemic Poly(L,D-lactide), PDLLA, is obtained when 50%L/50%D-units are incorporated at random.

It is well established that the properties of lactic acid based polymers vary to a large extent depending on the ratio between, and the distribution of, the two stereoisomers [6]. For instance, constituent properties of lactic acid polymers have been tailored by formation of different type *copolymers*, either formed by enantiomeric blocks [7] or by chains with non-random distributions of L and D units [8–10]. Lactic acid polymer properties can also be modified by forming blends of the two op-

tically pure enantiomeric polymers, either by solution casting [11–15] or melt blending [16, 17].

Lactic acid based polymers, when optically pure, use to crystallize from the melt in a pseudo-orthorhombic crystal (α form) with unit cell parameters $a = 1.07$ nm, $b = 0.59$ nm and $c = 2.78$ nm, and $\alpha = \beta = \gamma = 90^\circ$ [18], although β and γ polymorphs have also been reported respectively in stretched fibres [19] and when epitaxially crystallized on hexamethylbenzene [20]. The α crystal cell of lactic acid polymers is constituted by 10_3 helices in which ten monomer units intervene per three turns containing two helices that turn left or right, respectively for PLLA and PDLA [21, 22].

Since first reported by Ikada *et al.* [23], many studies have proved that racemate crystallites of lactic acid polymers, constituted by cells containing both enantiomeric chains, also called stereocomplex, melt at a significantly higher temperature than α or β polymorphs constituted of optically pure macromolecular segments [6]. The stereocomplex crystal form, hereafter called η , was found to crystallize in the triclinic system, with unit cell parameters $a = 0.916$ nm, $b = 0.916$ nm and $c = 0.870$ nm, and $\alpha = 109.2^\circ$, $\beta = 109.2^\circ$ and $\gamma = 109.8^\circ$ [21]. In this case, the chains constitute a 3_1 helix, and each unit cell contain segments of L-lactide and D-lactide chains [22]. Stereocomplex crystalline structures have been observed in enantiomeric lactic acid based copolymers [7, 10] and in enantiomeric PLA blends [23, 24] and are explained by the higher

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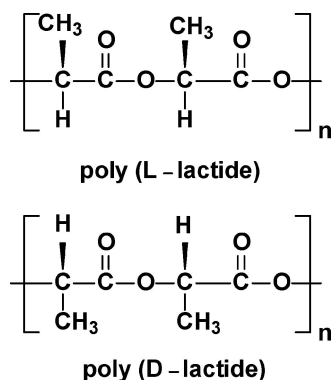


Figure 1 Structural unit of optically pure polylactides.

compaction induced by intramolecular or intermolecular interactions of lactic units of opposite configurations.

Regardless they are to be used in medical or ecological applications lactic acid polymer products and devices are preferably to be conformed by conventional melt processing techniques such as extrusion or injection moulding. Both the evolution of physical properties and biodegradability of polylactides depend on issues connected with crystallization developed during melt solidification.

Crystallization kinetics and melting behaviour of lactic acid polymers of different optical purity have been investigated in several studies [10, 25–31] in which it is found that the melting temperature and degree of crystallinity are dependent on the molar mass, thermal history and the purity of the polymer. However, processing related final properties are still to be further investigated to gain confidence in engineering design of lactic acid based polymer parts.

As expected for any thermoplastic material, physical and mechanical properties of lactic acid polymers are sensitive to the amount and type of crystallization, and to thermal degradation developed during processing. Therefore, some aspects of processing conditions can be considered to optimise the thermomechanical behaviour by means of the development of a desired microstructure. With this aim isothermal crystallizations have been carried out among a range of crystallization temperatures and times. Then, industrial-like cooling processes for conformation of parts such as full annealing, air quenching and water quenching have been simulated by non-isothermal crystallizations from the melt. The relationships between processing and crystallinity of polylactides are evaluated in this study. In a further work the mechanical behaviour of melt processed polylactides will be considered.

2. Experimental

2.1. Materials

The polylactides used in this study were supplied by PURAC BIOCHEM (Netherlands). Table I shows the values of the residual monomer content, the specific rotation in chloroform at 20°C, the intrinsic viscosity in chloroform at 25°C and the viscosimetric molecular weight calculated according to a Mark-Howink type equation for polylactide [26], $\eta = 5.45 \times 10^{-4} M_v^{0.73}$.

TABLE I Characteristics of polylactides

Material	RS (%)	RM (%)	α (deg)	$[\eta]$ (dl/g)	M_v (g/mol)
PLLA 1	<0.01	<0.1	-158.4	4.64	242000
PLLA 2	<0.01	<0.1	-157.3	5.74	323800
PDLA	<0.03	<0.2	+158.2	5.68	319400

RS: Residual Solvent; RM: Residual Monomer; α : Rotatory power in CHCl_3 at 25°C; $[\eta]$: Intrinsic viscosity; M_v : Molecular weight (viscous).

2.2. Melt blending

PLLA2 and PDLA pellets were melt processed in a laboratory mixer made up of a heated cavity and a rotor turning at 60 r.p.m. Temperature was held at 240°C for 5 min up to the rotary movement was stopped. Polylactide enantiomeric blends were then immediately extruded mechanically from the bottom die of the cavity using the rotor as a plunger. Table II summarizes the PLLA/PDLA compositions obtained by melt processing and their acronyms, to be used hereafter.

2.3. Isothermal and non isothermal crystallization of PLLA

PLLA1 samples were melted in a Perkin Elmer DSC-7 at 215°C for 1 min. Isothermal solidifications were performed by rapid cooling from the melt to the chosen crystallization temperatures, 70, 80, 90, 100, 120 and 150°C respectively, and holding there for four different times, 1 min, 15 min, 1 h and 24 h respectively. Non-isothermal continuous solidifications of PLLA1 samples after melting at 215°C for 1 min were also performed, at these cooling rates: 2, 4, 20, 40, 100 and 200°C/min.

Crystallization and melting behaviour of both isothermally and non-isothermally solidified PLLA samples were characterized in a subsequent DSC scan at a heating rate of 20°C/min. Melting temperature (T_m) and melting enthalpies (ΔH_m) were measured from the endothermic peaks shown by all samples studied; crystallization temperature (T_c) and crystallization enthalpies (ΔH_c) were also measured in samples showing during the scan an exothermic peak. Crystallinity degree of samples was calculated as follows:

$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \cdot 100 \quad (1)$$

in which X_c (%) is the degree of crystallinity in percentage calculated as the ratio of the neat melting enthalpy of the sample to the melting enthalpy value for a

TABLE II Polylactides obtained by melt processing and their acronyms

% wt. PLLA	% wt. PDLA	Acronym
100	0	PLLA
80	20	B-80L/20D
60	40	B-60L/40D
40	60	B-40L/60D
20	80	B-20L/80D
0	100	PDLA

100% crystalline PLLA. A value of $\Delta H_m^0 = 106 \text{ J/g}$ has been accepted according to the bibliography [10], even though smaller [25] and higher [34] values have also been proposed for 100% crystalline PLLA homocrystallites.

2.4. Non isothermal crystallization of PLLA/PDLA blends

Melt processed polylactides of Table I were cut in appropriate size and introduced in the DSC cell to remelt and crystallize under non-isothermal conditions. All PLLA/PDLA samples, pure enantiomeric polymers included, were heated to 240°C , hold there for 1 min and submitted to cool at $2^\circ\text{C}/\text{min}$, $40^\circ\text{C}/\text{min}$ or $200^\circ\text{C}/\text{min}$, in order to simulate respectively non-isothermal crystallization conditions for full annealing, air quenching and water quenching, during conformation of polylactide parts in a mould.

Crystallization and melting behaviour of these non isothermally crystallized PLLA/PDLA materials was determined in a subsequent DSC scan at a heating rate of $20^\circ\text{C}/\text{min}$. Degree of crystallinity was calculated using the values of $\Delta H_m^0 = 106 \text{ J/g}$ for PLA homocrystallites and $\Delta H_m^0 = 142 \text{ J/g}$ for stereocomplex crystallites [27].

3. Results and discussion

3.1. Crystallization behaviour of PLLA

Isothermal crystallizations of PLLA were performed in the DSC cell, after quenching from the melt to the chosen crystallization temperatures. Crystallization and melting behaviour of these samples were analysed, after fast cooling of the samples from selected crystallization temperature to room temperature, on a subsequent temperature run at $20^\circ\text{C}/\text{min}$. Fig. 2 shows the calorimetric curves of PLLA isothermally crystallized at 100°C for different times: 1 min, 15 min, 1 h and 24 h.

Similar DSC curves were also obtained for the rest of crystallization temperatures, 70, 80, 90, 120 and 150°C . Since no qualitative differences were found among the DSC curves for PLLA crystallized at different temperatures, the curves of isothermal crystallizations at 100°C will serve us to evaluate the thermal behaviour common to all crystallization temperatures studied here for PLLA. Quantitative differences in thermal properties found during the different isothermal crystallizations will be highlighted from values shown in Table III.

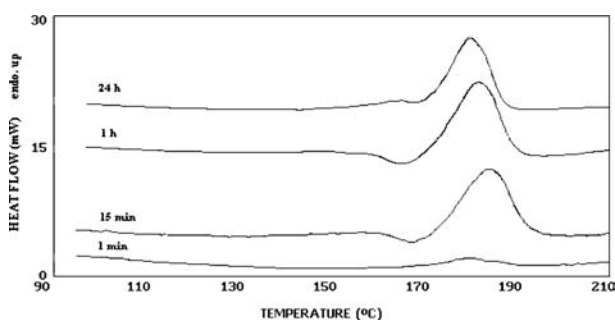


Figure 2 DSC curves of PLLA isothermally crystallized at 100°C .

TABLE III Thermal properties and Degree of crystallinity (X_c) of PLLA after isothermal crystallizations from the melt at different temperatures

Temperature (T_c)	Time	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	Crystallinity (%)
70°C	1 min	191.3	4.1	1.5
	15 min	191.3	3.2	2.2
	1 h	193.8	5.5	3.6
	24 h	193.0	38.0	19.3
80°C	1 min	190.2	3.3	1.9
	15 min	194.4	6.5	5.7
	1 h	198.2	16.6	9.5
	24 h	191.0	42.9	36.6
90°C	1 min	191.5	2.8	1.9
	15 min	191.7	26.0	9.2
	1 h	197.7	43.0	35.6
	24 h	191.3	39.9	34.9
100°C	1 min	193.0	4.1	2.1
	15 min	198.1	34.6	28.5
	1 h	197.7	36.1	29.2
	24 h	193.2	43.8	41.3
120°C	1 min	191.7	3.1	2.0
	15 min	192.2	5.0	4.7
	1 h	180.9	38.8	35.4
	24 h	201.7	57.1	53.9
150°C	1 min	194.4	3.0	1.7
	15 min	191.1	3.1	2.1
	1 h	195.5	4.8	3.5
	24 h	203.6	92.8	87.5

T_c = Selected crystallization temperature; T_m = Melting temperature; ΔH_m = Melting enthalpy

All curves of Fig. 2 show, regardless the time employed for crystallization, a clear endothermic heat flow behaviour between 170 – 195°C . This endothermic peak corresponds to the fusion of the PLLA crystalline structure and is determined, from the end-point of the peak at $\sim 195^\circ\text{C}$. This is considered the melting point of the PLLA crystallites developed with higher perfection during the isothermal crystallizations at 100°C . The melting temperature values reported here are somewhat higher than some of the melting temperature values reported in the bibliography for optically pure polylactides, but taken into account that the later were often determined from the peak centre rather than from its end-point value, the transition is unquestionably the same and is attributed to the fusion of PLA α homocrystallites.

Poorly crystallized polylactides use to show an exothermic transition during the subsequent DSC scan, centred at ~ 105 – 115°C , which is attributed to the crystallization of some amorphous regions that did not crystallize during the previous solidification process. For isothermal crystallizations performed at 100 and 90°C , rather than a complete exothermic peak an exothermic event just before melting occurs. This event has also been observed by other authors [10, 35] and has been attributed to the fusion of crystals of lower dimension which, recrystallizing, give the cited small exotherm deviation just prior to melting. It is to be noted too that, irrespective of the isothermal conditions employed, PLLA does not show any temperature crystallization peak at low temperatures, which indicates that isothermal crystallization conditions have been strong

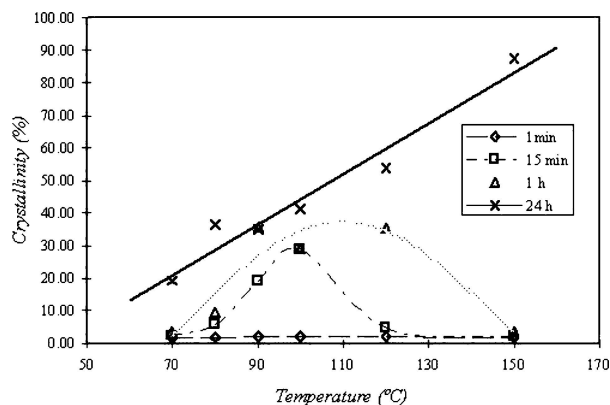


Figure 3 Evolution of PLLA crystallinity during isothermal crystallizations.

enough to avoid subsequent low temperature crystallization phenomena during the DSC scan.

Degree of crystallinity of PLLA has been calculated according to Equation 1, using the values of melting enthalpies obtained for each crystallization temperature and time selected (Table III). To calculate the actual degree of crystallinity in these cases, the correspondent exothermic enthalpy is subtracted from the endothermic melting enthalpy when samples crystallized during the scan. PLLA sample crystallized at 100°C for 24 h, for example, did not show any crystallization exotherm and therefore its crystallinity degree is determined as 41.3%, from the ratio of its melting enthalpy (43.8 J/g) to the melting enthalpy of a perfect PLLA homocrystallite (106 J/g). However, the 15 min crystallized sample showed a small crystallization just prior to melting at 166.1°C, with a crystallization enthalpy value of -3.9 J/g that must be subtracted to the melting enthalpy (34.6 J/g) and thus, according to Equation 1, we can calculate its neat crystallinity, this is $X_c = (34.6 - 3.9) \times 100/106 = 28.5\%$.

Equivalent DSC scans of those shown in Fig. 2 for PLLA crystallized at 100°C were performed for PLLA isothermally crystallized at 70, 80, 90, 120 and 150°C temperatures for 1 min, 15 min, 1 h and 24 h respectively. Quantitative values of the magnitudes associated with the crystallization and melting of PLLA at these temperatures can be also found in Table III.

Fig. 3 shows the evolution of crystallinity of PLLA developed during isothermal crystallizations at 70, 80, 90, 100, 120 and 150°C for different times (1 min, 15 min, 1 h, 24 h). For 24 h crystallized samples, a linear increase of PLA crystallinity is observed with crystallization temperature, reaching the value of 87.5% crystallinity at 150°C. However, for shorter crystallization times (1 h, 30 min and 1 min) the overall behaviour is not linear and it can be observed the well known effect of temperature on crystallization rate, this latter being maximum at a T_c intermediary between T_g and T_m .

The influence of crystallization temperature on PLLA crystallinity depends on nucleation and growth of crystallites at these temperatures. At high undercooling temperatures from the melt, for example at 70°C, a temperature a little higher than the T_g of PLLA (around 63°C), the conditions for diffusion and mobility of polymer chains are not favored so that, even if the thermo-

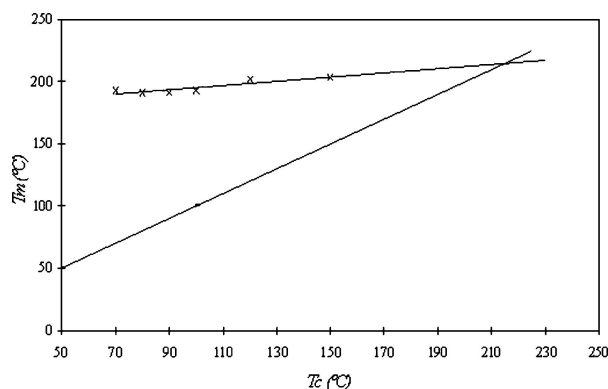


Figure 4 Determination of the thermodynamic melting temperature of PLLA from isothermal crystallizations at various temperatures.

dynamic driving force for nucleation of crystallites is high and thus it is expected a high density of small crystals, the overall development of crystallinity at this temperature is small. On the other corner, at low undercooling temperatures, for example at 150°C, the driving force is small but conditions for diffusion and mobility of polymer chains improve and therefore crystallinity increases. At intermediate crystallization temperatures there is a competition between thermodynamics and kinetics that explains why, for a given crystallization time, crystallinity degree evolution with temperature goes through a maximum.

It is well established that the melting temperature depends on perfection of polymer crystals developed under kinetic conditions [32]. Since PLLA crystals studied here have been developed under different isothermal crystallization temperatures and times their melting temperatures vary and are lower than the thermodynamic melting temperatures. However, using the extrapolation method of Hoffmann-Weeks [32, 33] in which the melting temperature is represented versus the crystallization temperature, the equilibrium melting temperature of a given polymer can be estimated by the intersection of the line connecting the different experimental points to the line constructed from the $T_m = T_c$ points. Fig. 4 shows the representation of the experimental equilibrium temperature versus the crystallization temperature used in PLLA crystallized for 24 h. Following to the above described method a value of 215°C is obtained as equilibrium melting point of PLLA.

3.2. Crystallization behaviour of PLLA/PDLA blends

Figs 5 and 6 show respectively the DSC curves of PLLA and PDLA after cooling from the melt at (a) 200°C/min, (b) 40°C/min and (c) 2°C/min. It can be observed that both optically pure polylactides show very similar behaviour: a single melting temperature peak at $\sim 190^\circ\text{C}$ that is attributed to the melting of polylactide α crystallites developed during the non-isothermal crystallization in the DSC. This melting peak is accompanied with a crystallization peak at $\sim 115^\circ\text{C}$ in samples cooled at 200 and 40°C/min, while there is no crystallization peak appearing in samples cooled at 2°C/min.

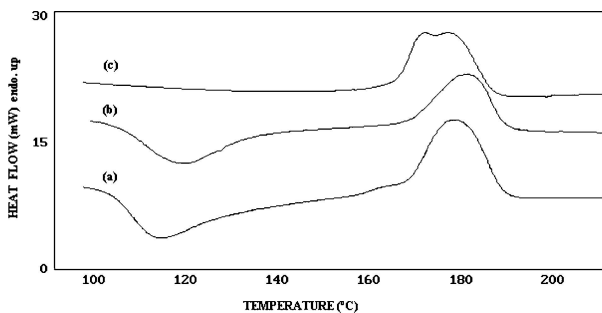


Figure 5 DSC curves of non-isothermally crystallized PLLA: (a) 200°C/min, (b) 40°C/min, (c) 2°C/min.

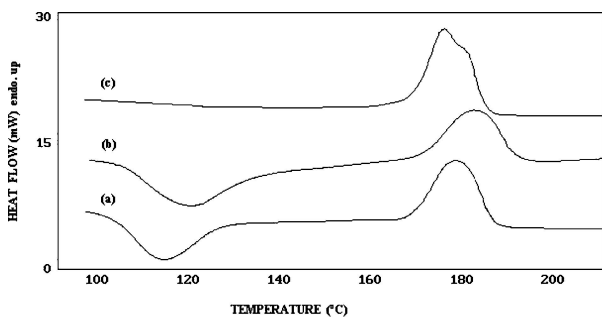


Figure 6 DSC curves of non-isothermally crystallized PDLA: (a) 200°C/min, (b) 40°C/min, (c) 2°C/min.

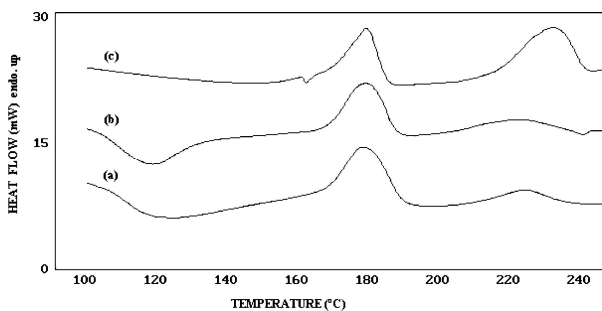


Figure 7 DSC curves of non-isothermally crystallized 50L/50D equimolar blend: (a) 200°C/min, (b) 40°C/min, (c) 2°C/min.

Fig. 7 shows the DSC curves of the equimolar PLLA/PDLA 50/50 blend after cooling from the melt at 2, 40 and 200°C/min. In this case, as in the case of non-blended PLLA or PDLA, there is also a crystallization exothermic peak appearing for 200°C/min and 40°C/min cooling rates, centred respectively at 124.7 and 118.6°C, while no crystallization peak is observed for samples cooled from the melt at 2°C/min.

The melting behaviour of B-50L/50D blend showed in Fig. 7 is revealed different from those of PLLA or PDLA since two endothermic peaks appear in the blend when a single melting was reported in Figs 5 and 6 for PLLA and PDLA respectively. From the end-point values of these two endothermic peaks appearing in the equimolar blend, a lower melting temperature around 190°C and a higher melting temperature around 240°C have been determined. The lower melting transition obtained for B-50L/50D blend is very close to that observed for crystals developed during isothermal and non isothermal crystallizations of optically pure PLLA and PDLA and therefore is attributed to the fusion of the α form polylactide crystals. The higher melting tran-

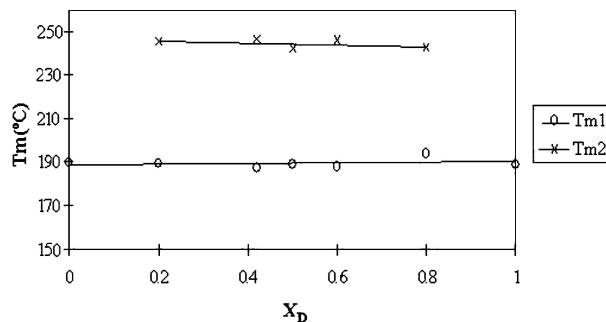


Figure 8 Melting temperature of α homocrystallites and η stereocomplex crystallites developed during non isothermal crystallization of PLLA/PDLA blends.

sition is similar to that obtained in the case of L- and D-enantiomer blends or copolymers of lactic acid [17, 23] and is attributed to the fusion of stereocomplex crystallites reported in these cases. Since both L- and D polylactide isomers used here for blending are optically pure, the high melting temperature value of 240°C obtained for the equimolar blend is in agreement with the lower value (230°C) found in stereocomplex crystals of an equimolar blend composed of optically pure PLLA and PDLA of 80% optical purity [17].

Similar DSC curves of those obtained for B-50L/50D blend were obtained for the rest of PLLA/PDLA blends studied: B-80L/20D, B-60L/40D, B-40L/60D and B-20L/80D. In fact, all of them showed a double melting behaviour, which is attributed to the separate fusion of the α and η form crystals. Fig. 8 represents the evolution of melting temperature of polylactides with blend composition. The data represented in this figure correspond to samples cooled at 2°C/min. The melting temperature evolution of the rest of samples cooled at higher rates was very similar and thus is not shown. From both T_{m1} and T_{m2} values reported in Fig. 8 it may be emphasized that melting temperature of both polylactide α and η crystals keeps nearly constant at ~ 190 and ~ 240 °C respectively and therefore it is not affected by blend composition.

As expected for conditions of crystallization under which polylactide crystals have been nucleated and grown during these non isothermal conditions, melting enthalpies obtained for all PLLA/PDLA compositions (Table IV) significantly increase when they are solidified at 2°C/min, compared to those crystallized at 40 and 200°C/min, indicating a higher crystallinity development at slow cooling rates, in agreement with higher crystallinity values observed for PLLA isothermal crystallizations at higher temperatures. Fig. 9 shows the evolution of melting enthalpies of PLLA/PDLA blends non-isothermally crystallized from the melt at 2°C/min. Melting enthalpies corresponding to the lower melting temperature homocrystallites and to the higher melting stereocomplex crystals are represented in function of % PDLA in the blend. As can be seen melting enthalpy of homocrystallites (ΔH_{m1}) decreases as PDLA fraction (X_D) increases in the blend, goes through a minimum at around an equimolar composition, and further increases to attain at $X_D = 1$ (PDLA) a similar value of that shown at $X_D = 0$ (PLLA). Melting enthalpy of stereocomplex

TABLE IV Thermal properties of non-isothermally crystallized PLLA, PDLA and their blends

Material	Cooling rate	T_c (°C)	ΔH_c (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	ΔH_m (J/g)	ΔH_m^0 (J/g)	X_c (%)
100L/0D	200°C/min	115.9	-35.5	191.3	40.4	-	-	4.9	106.0	4.6
	40°C/min	117.0	-36.5	196.9	39.2	-	-	2.6	106.0	2.5
	2°C/min	-	-	190.1	49.7	-	-	49.7	106.0	46.9
80L/20D	200°C/min	117.2	-26.3	192.9	32.1	239.0	6.3	12.2	121.5	10.0
	40°C/min	119.2	-20.2	194.1	33.3	235.8	5.0	18.2	121.5	15.0
	2°C/min	-	-	189.3	41.4	245.4	31.2	72.6	121.5	59.7
60L/40D	200°C/min	111.3	-27.0	195.0	31.1	243.3	14.6	18.7	128.6	14.6
	40°C/min	123.6	-26.3	190.8	32.9	236.9	7.5	14.2	128.6	11.0
	2°C/min	-	-	187.6	29.4	246.5	49.8	79.2	128.6	61.6
50L/50D	200°C/min	129.4	-28.2	192.7	30.4	244.4	14.0	16.2	125.5	12.9
	40°C/min	116.5	-27.5	190.5	32.2	239.0	18.8	23.5	125.5	18.7
	2°C/min	-	-	189.1	33.1	242.4	39.0	72.2	125.5	57.5
40L/60D	200°C/min	113.8	-31.1	194.2	31.6	246.0	13.5	14.0	125.9	11.1
	40°C/min	112.6	-23.4	195.9	30.5	236.7	6.5	13.5	125.9	10.8
	2°C/min	-	-	188.0	34.4	246.2	42.6	77.0	125.9	61.2
20L/80D	200°C/min	124.7	-32.5	194.4	34.6	239.5	7.8	9.9	116.8	8.5
	40°C/min	119.2	-33.3	197.8	34.8	242.3	1.8	3.2	116.8	2.7
	2°C/min	-	-	194.0	47.4	242.8	20.2	67.5	116.8	57.8
0L/100D	200°C/min	113.1	-32.5	191.2	40.6	-	-	8.1	106.0	7.6
	40°C/min	118.6	-33.7	197.0	37.0	-	-	3.3	106.0	3.1
	2°C/min	-	-	188.7	45.4	-	-	45.4	106.0	42.8

T_c : Crystallization temperature; ΔH_m : Crystallization enthalpy; T_m : Melting temperature; ΔH_m : Melting enthalpy; ΔH_m^0 : Standard melting enthalpy according to Equation 3; X_c : Crystallinity degree

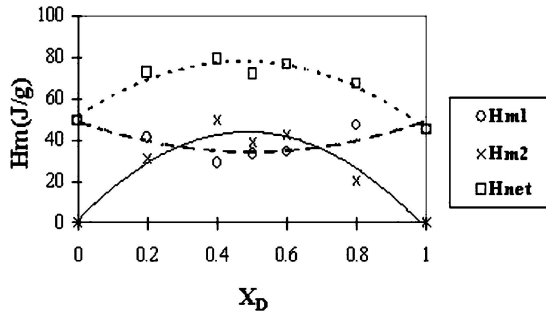


Figure 9 Melting enthalpies of poly(lactide)'s α homocrystals (H_{m1}) and η stereocomplex crystals (ΔH_{m2}), and neat enthalpy, developed during solidification at 2°C/min.

crystallites, contrarily, increases with PDLA fraction in the blend, goes through a maximum around an equimolar composition, and further decreases to zero at $X_d = 1$ (PDLA). The overall melting enthalpy values are also represented in this figure. As can be observed the neat melting enthalpy progresses from 49.7 J/g for PLLA to a maximum of 79.2 J/g at intermediate blend compositions to further decrease to 45.4 for PDLA.

Table IV summarizes the thermal properties of PLLA, PDLA and their 80L/20D, 60L/40D, 50L/50D, 40L/60D, 20L/80D blends. In this table both melting temperatures and their corresponding enthalpies for PLLA/PDLA blends are reported with subscripts 1 and 2 respectively for α homocrystallite and η stereocomplex crystals melting; since non-blended PLLA and PDLA crystallize under α form, their transitions are reported with subscript 1.

Overall crystallinities (X_c) of non-isothermally crystallized optically pure polylactides and their blends are reported in Table IV. X_c was calculated as follows:

$$X_c(\%) = \frac{\Delta H_{m1} + \Delta H_{m2} - \Delta H_c}{\Delta H_{m(\text{blend})}^0} \cdot 100 \quad (2)$$

$\Delta H_{m(\text{blend})}^0$ is the theoretical value of melting enthalpy for PLA perfect crystals; since this theoretical enthalpy value is different for poly(lactide) α form crystallites (106 J/g) and η form crystallites (142 J/g), it can be postulated that this value varies with the relative amount of both α and η crystal forms in the following manner:

$$\begin{aligned} \Delta H_{m(\text{blend})}^0 &= \Delta H_{m(\text{homocrystallite})}^0 \cdot X_{\text{homocrystallite}} \\ &+ \Delta H_{m(\text{stereocomplex})}^0 \cdot X_{\text{stereocomplex}} \end{aligned} \quad (3)$$

$X_{\text{homocrystallite}}$ and $X_{\text{stereocomplex}}$ are respectively the relative amounts of both α and η type crystals developed during the non-isothermal crystallizations, and can be calculated, in the case of no crystallization exotherm appearing during the DSC scan, from the enthalpy values as follows:

$$X_{\text{homocrystallite}} = \frac{\Delta H_{m1}}{\Delta H_{m1} + \Delta H_{m2}} \quad (4)$$

$$X_{\text{stereocomplex}} = \frac{\Delta H_{m2}}{\Delta H_{m1} + \Delta H_{m2}} \quad (5)$$

The evolution of overall crystallinity calculated from Equation 2 reported in Table IV also shows a maximum value at intermediate blend compositions for each of the selected non-isothermal crystallizations. This is attributed to the partial development of crystallization of poly(lactides) in the form of η stereocomplex. Table V shows the stereocomplex content developed by PLLA/PDLA blends crystallized during solidification at 2°C/min. As it has been observed before, PLLA/PDLA blends solidified at 40° and 200°C/min did show a single crystallization exothermic peak during the DSC scan, from which it was not possible to separate crystallization corresponding to α and η

TABLE V Stereocomplex content of PLLA/PDLA blends crystallized at 2°C/min from the melt

Material	% Stereocomplex
PLLA	0
B-80L/20D	43.0
B-60L/40D	62.9
B-40L/20D	55.3
B-20L/80D	29.9
PDLA	0

form crystals; therefore stereocomplex content has not been calculated for high cooling rate non-isothermally crystallized samples. It can be observed in this table that blend compositions that are close to equimolar composition (B-60L/40D and B-40/60L/D) show values higher than 50% stereocomplex, which indicates a preferential crystalline development of polylactide as η polymorph. On the other hand, B-80L/20D and B-20L/80D blends show a lower content of stereocomplex, indicating a preferential development of α crystalline form at these compositions.

Having a look to the crystallinities shown in Table IV for PLLA/PDLA samples crystallized at 2°C/min, it is also worth to mention that there is a significant increase of crystallinity in PLLA/PDLA blends compared to the crystallinities of non-blended optically pure PLLA or PDLA. All blends show an overall crystallinity degree close to 60%, while PLLA or PDLA hardly get to 45%. This may be attributed to two phenomena. In a first instance it seems that there is a preferential development of polylactides to crystallize as η stereocomplex at crystallization conditions approaching close to thermodynamic equilibrium for the melting of form α . Second, since η stereocomplex crystals have higher melting temperature than α crystallites it seems reasonable to predict that η stereocomplex crystals would be formed first and thus they could act as sites for heterogeneous nucleation of α homocrystallites, contributing this way to an increase of the neat crystallinity degree.

4. Conclusions

Isothermal and non-isothermal crystallizations have been performed from the melt for PLLA, PDLA and PLLA/PDLA blends leading to the following conclusions:

(1) Non-blended optically pure PLLA and PDLA crystallize as α homocrystallites irrespective the crystallization conditions employed. Crystallinity degree of PLLA varied from nearly amorphous to 87%, depending on the isothermal temperature and time employed. Non-isothermally crystallized PLLA crystallinities ranged from nearly amorphous to 47%.

(2) Melting temperatures of PLLA and PDLA samples were determined as 195°C from the end-point melting peak value. Following to Hoffmann and Weeks method the equilibrium melting temperature of polylactide α crystal is foreseen at 215°C.

(3) Non-isothermal crystallizations from the melt of PLLA/PDLA blends, contrary to the non-blended sam-

ples, show double melting behaviour. This behaviour is attributed to a separate melting of polylactide as α and η crystal polymorphs. Both type of crystals are found in all blends at more or less amount depending on the blend composition and the cooling rate from the melt employed during crystallization.

(4) PLLA/PDLA blends show higher neat melting enthalpy values and crystallinities than non-blended optically pure PLLA or PDLA when crystallizations were performed at slow cooling rates. These results suggest a preferential crystallization of polylactide as η stereocomplex at conditions close to thermodynamic equilibrium for the melting of form α and the possibility of η crystals to act as nucleation sites for development of α crystals.

(5) It would be interesting to attain a selective crystallization of polylactide as 100% η stereocomplex in order to study its physical, mechanical and biodegradation properties.

Acknowledgements

This work has been made possible by a financial support of *Universidad Pública de Navarra* and the *Ministerio de Industria y Energía*. We do not forget Professor Jaime Faustmann (r.i.p.) for his initial support.

References

- O. M. BÖSTMAN, *J. Bone Joint Surg.* **73-A**(1) (1991) 148.
- R. G. SINCLAIR, *J. Macromol. Sci-Pure Appl. Chem.* **A33** (1996) 587.
- E. T. H. VINIK, K. R. RÁBAGO, D. A. GLYSNER and P. R. GRUBER, *Polym. Degrad. Stab.* **80** (2003) 403.
- S. KARLSSON and A. C. ALBERTSSON, *Polym. Eng. Sci.* **38** (1998) 1251.
- R. T. MACDONALD, S. P. MCCARTHY and R. A. GROSS, *Macromolecules* **29** (1996) 7356.
- A. SÖDERGARD and M. STOLT, *Prog. Polym. Sci.* **27** (2002) 1123.
- N. YUI, P. J. DIJKSTRA and J. FEIJEN, *Makromol. Chem.* **191** (1990) 481.
- F. CHABOT, M. VERT, S. CHAPELLE and P. GRANGER, *Polymer* **24** (1983) 53.
- M. WISNIEWSKI, A. LEBORGNE and N. SPASSKI, *Makromol. Chem. Phys.* **198** (1997) 1227.
- J. R. SARASUA, R. E. PRUD'HOMME, M. WISNIEWSKI, A. LE BORGNE and N. SPASSKI, *Macromolecules* **31** (1998) 3895.
- H. TSUJI, F. HORII, S. H. HYON and Y. IKADA, *ibid.* **24** (1991) 2719.
- H. TSUJI, S. H. HYON and Y. IKADA, *ibid.* **24** (1991) 5657.
- H. TSUJI, S. H. HYON and Y. IKADA, *ibid.* **25** (1992) 2940.
- H. TSUJI and Y. IKADA, *ibid.* **24** (1992) 5719.
- H. YAMANE and K. SASAI, *Polymer* **44** (2003) 2569.
- H. TSUJI and Y. IKADA, *Macromolecules* **26** (1993) 6918.
- S. BROCHU, R. E. PRUD'HOMME, I. BARAKAT and R. JERÔME, *ibid.* **28** (1995) 5230.
- P. DE SANTIS and A. J. KOVACS, *Biopolymers* **6** (1968) 209.
- B. ELING, S. GOGOLEWSKI and A. J. PENNING, *Polymer* **23** (1982) 1587.
- L. CARTIER, T. OKIHARA, Y. IKADA, H. TSUJI, J. PUIGGALI and D. LOTZ, *ibid.* **41** (1990) 8909.
- T. OKIHARA, M. TSUJI, A. KAWAGUCHI, K. KATAYAMA, H. TSUJI, H. HYON and Y. IKADA, *J. Macromol. Sci. Phys.* **B30** (1991) 119.
- D. BRIZZOLARA, H. J. CANTOW, K. DIEDERICKS, E. KELLER and A. J. DOMB, *Macromolecules* **29** (1996) 91.

23. Y. IKADA, K. JAMSHIDI, H. TSUJI and S. HYON, *ibid.* **20** (1987) 904.
24. H. TSUJI and Y. IKADA, *Polymer* **40** (1999) 6699.
25. E. W. FISCHER, H. J. STERZEL and G. WEGNER, *Kolloid Z u Z Polymere* **251** (1973) 980.
26. A. SCHINDLER and D. HARPER, *J. Polym. Sci. Polym. Chem. Ed.* **17** (1979) 2593.
27. G. L. LOOMIS, J. R. MURDOCH and K. H. GARDNER, *Polymer. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **31** (1990) 55.
28. K. JAMSHIDI, S. H. HYON and Y. IKADA, *Polymer* **29** (1988) 2229.
29. R. VASANTHAKUMARI and A. J. PENNING, *ibid.* **24** (1983) 175.
30. H. ABE, Y. KIKKAWA, Y. INOUE and Y. DOI, *Biomacromolecules* **2** (2001) 1007.
31. J. HUANG, M. S. LISOWSKI, J. RUNT, E. S. HALL, R. T. KEAN and N. BUEHLER, *Macromolecules* **31** (1998) 2593.
32. B. WUNDERLICH, "Macromolecular Physics" (Academic Press 1990) Vol 3.
33. J. D. HOFFMAN and J. J. WEEKS, *J. Res. Nat. Bur. Std.* **66A** (1962) 13.
34. D. K. GILDING and A. M. REED, *Polymer* **29** (1979) 1459.
35. S. IANNACE, A. MAFEZZOLI, G. LEO and L. NICOLAIS, *ibid.* **42** (2001) 3799.

*Received 17 November 2004
and accepted 5 January 2005*