

Effect of Nucleating Agents on the Molar Mass Distribution and Its Correlation with the Isothermal Crystallization Behavior of Poly(L-lactic acid)

Maurizio Penco,¹ Gloria Spagnoli,¹ Isabella Peroni,¹ M. Arifur Rahman,^{1,2} Marco Frediani,³ Werner Oberhauser,⁴ Andrea Lazzeri²

¹Department of Mechanical and Industrial Engineering, University of Brescia, Via Valotti 9, 25123 Brescia, Italy

²Department of Chemical Engineering, Industrial Chemistry and Materials Science, University of Pisa, Via Diotisalvi 2, 56126 Pisa, Italy

³Department of Chemistry, Via della Lastruccia 13, 50019, Sesto F.no, Florence, Italy

⁴Institute of Chemistry and Organometallic Composite-Centre for National Research (ICCOM-CNR), Area di Ricerca CNR di Firenze, via Madonna del Piano 10, 50019 Sesto, Fiorentino, Italy

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ABSTRACT: In this work, the effect of the processing conditions on the thermal behavior of a commercial poly(L-lactic acid) (PLLA) was investigated. In particular, PLLA having a very high molecular weight was processed by a discontinuous mixer at different mixing conditions. The molar mass variation was investigated by size exclusion chromatography–multiangle laser light scattering chromatography, and the thermal characteristics were detected by the conventional differential scanning calorimetry and dynamic mechanical thermal analysis. Tensile tests were performed at room temperature and at 60°C. Our attention was essentially focused on the crystallization behavior of the various samples obtained. A modest decline in the molar mass was obtained with two mixing

temperatures of 210 and 250°C, but a significant increase in the crystalline phase content was noticed, with a concomitant tremendous increment in the crystallization rate. A correlation was also made between the molar mass distribution and crystallization rate in isothermal conditions, where clearly visible were the effects of the processing temperature on both the molar mass distribution and how the nucleating agents affected the crystallinity of PLLA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3528–3536, 2011

Key words: crystallization; nucleation; differential scanning calorimetry (DSC); X-ray diffraction

INTRODUCTION

In this era of green science and technology, we are more concerned about materials that are environmentally benign, more precisely, materials that do not have a negative impact on nature. This is why biodegradability is considered as the prime concern in the production of most industrial products. Poly(lactic acid) (PLA) $\{-[\text{CH}(\text{CH}_3)\text{COO}]_n-\}$ is a biodegradable and biocompatible semicrystalline polymer that can be produced from renewable resources, such as corn.¹ It must be emphasized that the concomitant presence

and their molar ratio of the two enantiomeric species in PLA strongly affect the morphology of the material; that is, poly(L-lactic acid) (PLLA) is a semicrystalline polymer, and D,L-PLLA is an amorphous material.² The stereocomplexation between PLLA and poly(D-lactic acid) was performed as an effective method for increasing the thermal stability of PLLA-based materials.^{3,4} However, the production cost of poly(D-lactic acid) is the bottleneck of stereocomplexed PLLA materials. Commercially available PLA grades are obtained by the ring-opening polymerization of lactide, a dimer of lactic acid. Lactic acid is optically active and, thus, can be of L or D form. The maximum attainable crystallinity level is obtained by minimization of the amount of D-lactide isomers and L,D-lactide (i.e., mesolactide), in which the L-lactide is used as the major monomer.⁵ The crystallinity and crystallization rate obviously decrease as the purity in the crystallizable L-lactic acid segment decreases. For example, the crystallization half-time ($t_{1/2}$) was found to increase by roughly 40% for every 1 wt % increase in the mesolactide content of the polymerization mixture.⁶ Even at high L-lactic acid contents, however, PLA

Correspondence to: M. Penco (maurizio.penco@ing.unibs.it).

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crystallization is typically too slow to develop significant crystallinity unless the crystallization is induced by strain, such as in processes used to produce biaxially oriented films or bottles. In processes such as injection molding, where the orientation is limited and the cooling rate is high, it is much more challenging to develop significant crystallinity, and thus, formulation or process changes are required. This is why the crystal structure and crystallization behavior of PLLA have been extensively investigated by many techniques from the academic viewpoint of structural interest and for practical applications.^{7–13}

The polyester nature of PLLA produces a high thermal susceptibility of the material, in particular during melt processing, and significant molar mass variation results. This is why the understanding of the crystallization kinetics is an important concern in the design of PLLA-based materials with desirable properties through the control of the crystallization factors in PLLA. Despite extensive studies of PLLA, its crystallization behavior and crystal structure are still not completely understood. Depending on the processing conditions, PLLA can crystallize in α , β , or γ forms.^{7,8} The different crystalline morphologies can affect the chemical stability, physical/mechanical properties, and degradation rates⁹ in biodegradable polymers. Therefore, a thorough understanding of the crystallization behavior of PLLA is crucial.

The fine details of the isothermal and nonisothermal crystallization behaviors of PLLA have been analyzed by a number of research groups.^{11–13} The spherulite growth rate of PLLA in a wide temperature range, from 70 to 165°C, has been determined.^{11,13,14} The most peculiar behavior is a discontinuity in the crystallization kinetics of PLLA around 100–120°C. The crystallization rate of PLLA is very high at temperatures between 100 and 120°C, showing a clear deviation from the usual bell-shaped curve of polymer crystal growth. This discontinuity was correlated to a transition in the regime II–III growth of spherulites that was observed in the same temperature range.¹² However, Ohtani et al.¹⁴ proposed that crystal polymorphism may be responsible for the unusual crystallization behavior of PLLA. From wide-angle X-ray diffraction data, they concluded that when amorphous PLLA was crystallized at a temperature below 120°C, crystallites of the β form were produced, and when it was annealed at a temperature above 120°C, crystallites of the α form grew. Just recently, Di Lorenzo¹³ argued that this discontinuity might be ascribed to a sudden acceleration in spherulite growth, not associated with morphological changes in the appearance of PLLA spherulites because the powder diffraction patterns of the β and α forms are actually quite similar.

Zhang and coworkers^{15–17} recently reported the isothermal crystallization behavior of PLLA from the

melt and glassy states investigated by IR spectroscopy. They observed a significant difference between the spectral changes during the cold crystallization and melt crystallization processes of pure PLLA; this indicated that different crystal modifications might have been formed. The band splitting induced by the dipole–dipole interaction of CH₃ or C=O groups was observed only in the melt crystallization process, whereas in the cold crystallization process, no band splitting was observed. The result strongly suggests that different chain packing forms or intermolecular interactions exist during these two isothermal crystallization processes. However, the IR spectra of polymers, in general, are said to reflect the local structures and are presumably unaffected by the size and shape of the crystals or the morphology.¹⁸

The most viable method for controlling the crystallinity of PLA is to add a nucleating agent that will lower the surface free-energy barrier toward nucleation and, thus, initiate crystallization at higher temperatures upon cooling.¹⁹ Relatively few studies have focused on the nucleating agents for PLA. Clay was used by Okamoto et al.,²⁰ who found that the overall crystallization rate and spherulitic texture of PLA were strongly influenced by montmorillonite particles. At the same time, they found that the blending of low-molecular-weight aliphatic acid also increased the crystallization rate.²¹ Anderson and Hillmyer²² compared the nucleation efficiency of stereocomplex crystallites and the common nucleating agent talc. It was found that with 6 wt % talc, $t_{1/2}$ of PLA at 120°C was less than 1 min, but stereocomplex crystallites were even more effective. Hiltner and coworkers^{23,24} and Pluta²⁵ believed that the blending of poly(ethylene glycol) accelerated the crystallization of PLA and that decreasing the amount of poly(ethylene glycol) in the blend decreased the crystallization rate of PLA. Some other fillers (e.g., CaCO₃, hydroxyapatite, calcium hydrogen phosphate, bioactive glass, bishydrazides) were also investigated^{26–29} but only for mechanical properties.

In this study, PLLA was prepared in two different temperature conditions, and also, two different nucleating agents were used to control the crystallization of PLLA. The aim of this study was to investigate the isothermal crystallization behavior of PLLA with an Avrami equation because the isothermal crystallization kinetics could be better visualized through evaluation of the degree of crystalline conversion as a function of time at a constant temperature. There was also an attempt to correlate the dynamic mechanical behavior of the PLLA with its crystallization kinetics. An X-ray powder diffraction (XRPD) method was used to analyze the crystal structure of PLLA, and its crystallization behavior was studied by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

PLLA was purchased from Natureworks (Blair, NE) and had a nominal weight-average molecular weight (M_w) of 199,590 Da and the brand name 2002D. The material was dried at 60°C in vacuum (1 mmHg) for 4 days before use. Sodium benzoate ($\text{NaC}_6\text{H}_5\text{CO}_2$) and talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] were purchased from Fluka (Italy); both products were dried at 80°C *in vacuo* for 2 days.

Sample preparation

The dried PLLA was treated at two different temperatures (210 and 250°C) in a discontinuous mixer (Brabender, Plastograph, Duisberg, Germany) with a screw speed of 80 rpm, and the total mixing time was 10 min. The same screw-speed profile and mixing time were followed to mix starting PLLA (i.e., untreated PLLA) with both nucleating agents in the Brabender mixer. The total polymer content inside the mixing chamber was 50 g, and three different weight percentages of nucleants with respect to the total amount of PLLA were used to prepare nucleants containing PLLA.

Molecular characterization of PLLA

The molecular weight distribution of the PLLA materials was obtained by a multiangle laser light scattering (MALS) photometer online with a size exclusion chromatography (SEC) system. The SEC-MALS system consisted of an Alliance chromatographic system from Waters (Milford, MA), a MALS Dawn DSP-F photometer from Wyatt (Santa Barbara, CA), and a differential refractometer (Waters model 2414) used as concentration detector. This multidetector SEC-MALS system was described in detail elsewhere.^{9,30} The SEC column set was composed of two PLGel Mixed C columns (particle size = 5 μm) from Polymer Laboratories. The experimental conditions consisted of tetrahydrofuran as the mobile phase, a temperature of 35°C, and a flow rate of 0.8 mL/min. The calibration constant of the MALS photometer was calculated with toluene as a standard with the assumption of a Rayleigh factor of $1.406 \times 10^{-5} \text{ cm}^{-1}$. The MALS angular normalization was performed by measurement of the scattering intensity of a very narrow low-molecular-weight polystyrene standard [$M_p = 10.3 \text{ kg/mol}$, $R_g = 2.6 \text{ nm}$, M_w /number-average molecular weight (M_n) = 1.03; where M_p is peak molecular weight.] in the mobile phase, which was assumed to act as an isotropic scatterer. The refractive-index increment of the polymer with respect to the solvent at 25°C was measured by a KMX-16 differential refractometer from LDC Milton Roy (Rochester, NY).

XRPD

XRPD spectra were acquired with (PANalytical B.V. Lelyweg, The Netherlands) a PANalytical X'PERT PRO powder diffractometer, employing Cu K α radiation ($\lambda = 1.54187 \text{ \AA}$) and a parabolic mirror positioning device (MPD) mirror. The thermodiffraction study was carried out in an Anton Paar (HTK 1200) high-temperature reaction chamber under nitrogen. All spectra were acquired in a 2θ range from 5 to 40° with a step size of 0.0131° and a counting time of 18.9 s. Before the samples were heated, an XRD spectrum of each blend was obtained. Then, the blends were heated in the reaction chamber to 180°C by application of a heating rate of 10°C/min. The latter temperature was maintained for 4 min and was followed by the acquisition of XRD spectra. Afterward, the samples were cooled to 105°C with a cooling rate of -50°C/min, and they were maintained at the latter temperature for 45 min to acquire the XRD spectra in a time interval of 15 min. The samples were thereafter cooled to room temperature, and a final XRD spectrum of each blend was obtained at the latter temperature.

Mechanical properties

To perform the tensile test, the blend samples were dried at 80°C in a vacuum oven for 24 h. Mechanical tensile tests were performed with an Instron dynamometer (model 3366; High Wycombe, England) at two different temperatures (25 and 60°C) and at a crosshead rate of 10 mm/min (nominal strain rate = 0.1/min) on test pieces 100 mm in length (distance between grips $\approx 60 \text{ mm}$) and 10 mm in width. The thickness of the specimen was $2 \pm 0.1 \text{ mm}$. ASTM D 882 was followed for the tensile test.

Isothermal crystallization studies by conventional DSC

Thermal analysis was performed in a nitrogen atmosphere (50 mL/min) with a TA Instruments differential scanning calorimeter (DSC Q100; New Castle, DE) on samples of $7.5 \pm 0.3 \text{ mg}$ at a constant heating rate (q_h) of 10°C/min. The glass-transition temperature (T_g) was taken as the inflection point of the change in heat capacity.

The sample was quenched to the isothermal temperature of 105°C and kept at this temperature during various annealing periods of time. At the end of the isothermal step, another heating scan was run at 10°C/min from 20 to 200°C. The crystallization fraction obtained for an isothermal time t [$X(t)$] was calculated with the following equation [Eq. (1)]:

$$X(t) = [\Delta H_m(tt) - \Delta H_c(tt)] / \Delta H_m(t = 24 \text{ h}) \quad (1)$$

where $\Delta H_m(tt)$ is the fusion enthalpy obtained in the subsequent heating step after an isothermal time t ,

TABLE I
Molecular Masses and Thermal Characteristics of PLLA Samples Studied

Sample	Processing temperature (°C)	Talc (wt %)	Sodium benzoate (wt %)	M_n (Da)	M_w (Da)	D	T_g (°C) ^a	T_m (°C) ^a	ΔH_m (J/g) ^a
PLLA-1	Untreated	—	—	162,940	199,590	1.2	62 ± 0.5	151.5 ± 0.1	41.87
PLLA-2	250	—	—	119,040	153,990	1.3	61 ± 0.5	151.3 ± 0.1	50.08
PLLA-3	210	—	—	127,640	163,310	1.3	63 ± 0.5	151.9 ± 0.1	42.55
Blend 1	210	0.3	—	108,940	150,320	1.4	62 ± 0.5	152.0 ± 0.1	40.02
Blend 2	210	—	0.2	95,070	127,520	1.3	61 ± 0.5	150.1 ± 0.1	43.48
Blend 3	210	0.3	0.2	82,930	117,990	1.4	61 ± 0.5	150.0 ± 0.1	44.89

^a Values obtained after a isothermal time of 24 h at 105°C, starting from the melt status. The values of T_g and T_m were estimated with error levels of ±0.5 and ±0.1, respectively.

$\Delta H_c(tt)$ is the crystallization enthalpy during the subsequent heating step, and $\Delta H_m(t = 24 \text{ h})$ is the fusion enthalpy after an isothermal time of 24 h.

RESULTS AND DISCUSSION

Effect of the processing temperature and nucleating agents on the molar mass distribution

The mechanical response of the thermoplastic polymers is highly influenced by the molar mass, chain entanglements, chain alignment, and degree of crystallinity.³¹ The effect of the mixing temperature and nucleating agents on the molar mass distribution of the starting PLLA with an M_w of 199,500 Da and a polydispersity of 1.2 (PLLA-1) is shown in Table I. A significant decrease in the molecular weight was observed when high processing temperatures (210 and 250°C) were used. Pure PLLA processed at 250°C (PLLA-2) and 210°C (PLLA-3) showed a decline in the molar mass in comparison with that of pure PLLA. This was due to the high shear stress introduced by the rotation of screws inside the discontinuous mixer, and this shear stress strongly affected the molar mass distribution of PLLA. Very few works have been done on the effect of mechanical stress on the molar distribution of PLLA, which is a very important concern from a technological point of view. Early work in understanding the response of polymeric materials to mechanical stress was published by Staudinger and Bondy,³² who observed a decrease in the molecular weight of polymers in response to mastication. These results obviously suggest an accurate selection not only of the processing temperature but also of the profile of the screw and revolution rates for limiting the mechanical degradation processes inside the discontinuous mixing machine.

The change in the molar mass distribution was also influenced by the incorporation of nucleating agents in the PLLA matrix. The use of 0.3 wt % talc produced a significant decrease in the molecular weight of PLLA when it was treated at 210°C (Table I). The molar mass of the materials decreased from

163,300 Da (PLLA-3) to 150,300 Da (blend 1); the polydispersity increased from 1.3 to 1.4, respectively. Thus, the effect of talc on the molar distribution of PLLA was clearly evident. It is important to note here that talc is a phyllosilicate, and the crystals of this phyllosilicate [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] mineral have a high aspect ratio and few possible reactive sites located on the side steps³³ [Fig. 1(a,b)]. In fact, if a continuous sheet of silica rings is attached to both sides of a magnesia layer, the planar talc structure results [Fig. 1(a)]. Because both sides of this structure expose an oxide surface, individual talc plates are held together only by weak van der Waals forces.³⁴ The incorporation of talc into PLLA promoted the hydrolytic degradation of PLLA during the melt mixing because of the presence of OH groups in the side chain of talc, and thus, we observed a decline in the molar mass of PLLA.

On other hand, a higher decline in the molar mass distribution of PLLA was observed when sodium benzoate (0.2 wt %) was used as a nucleating agent for PLLA, and M_w of PLLA decreased from 163,300 (PLLA-3) to 127,500 Da (blend 2 in Table I); an analogous polydispersity was observed.

In fact, sodium benzoate is a weak base. Legras et al.³⁵ reported that the mechanism of action of organic nucleating agents such as sodium benzoate and its derived salts completely differed from the generally accepted model, at least in the case of polyesters. The nucleating agent reacted as a true chemical reagent with the molten macromolecules and

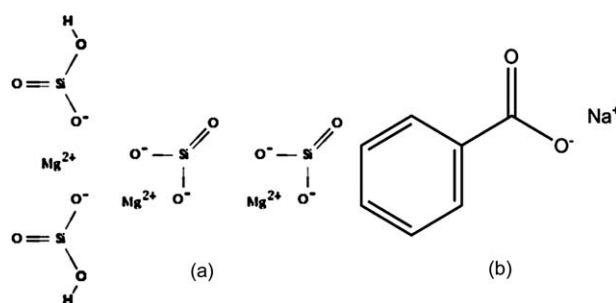


Figure 1 Chemical structures of (a) talc and (b) sodium benzoate.

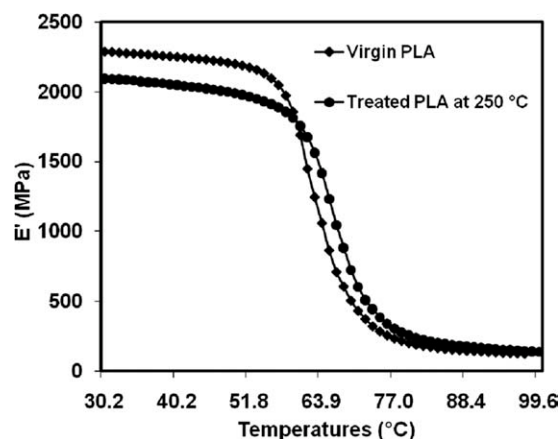


Figure 2 Dynamic mechanical thermal analysis curve for the starting PLLA and PLLA treated at 250°C, showing variation in E' .

produced ionic end groups that constituted the true nucleating species. We presume that the nucleation effect of sodium benzoate proceeded through the decomposition of the salt and the reaction of the benzoate ion with the acid end groups of the PLLA; another possibility was that sodium benzoate could have also promoted a hydrolytic effect on the polyester chain of PLLA.

When both of the nucleants were added, a higher decrease of molar mass (blend 3 in Table I) was observed, and the polydispersity was analogous to the sample containing only talc. In principle, nucleating agents, along with the processing conditions, affected the molar mass distribution of PLLA and, consequently, affected the crystallization behavior of PLLA. In general, lower molar masses produce higher amounts of crystalline phase and faster crystallization processes, but a significant loss of the mechanical properties can also occur. On the other hand, the use of talc and/or sodium benzoate promoted a higher decrease in the molar mass but a lower increase in the crystallinity in comparison with the starting PLLA. This suggests that nucleants produced a higher decline in the molar mass, but they disturbed the system in such a way that they limited the crystallinity degree at equilibrium (Table I, blends 1–3). The melting temperatures (T_m 's) of the starting PLLA (without nucleating agents) and two processed PLLAs (PLLA-2 and PLLA-3) varied

in the range 151.3–152.0°C (Table I). However, a decrease in T_m (ca. 2°C) of PLLA was observed when sodium benzoate was introduced (blends 2 and 3 in Table I). This was probably due to the fact that sodium benzoate acted as an impurity that produced some defects in the crystalline networks of PLLA.

T_g of the amorphous phase of PLLA did not show a significant variation when the molar mass of the materials changed in the range explored (Table I). In fact, the value of T_g was always in the range 61–63°C for all samples. This also suggested that the materials having lower molecular weight may have had a sufficiently high molar mass to be in the asymptotic portion of the T_g versus M_w trend (valid generally for completely amorphous polymers). On the other hand, higher crystallinity should increase the amount of a more rigid glassy phase portion near the crystalline domains, but generally this effect can not be detected easily, like a second higher T_g . Dynamic mechanical thermal analysis confirmed these results, and a higher storage modulus (E') was observed at the temperature above T_g for the samples having a higher crystallinity (Fig. 2).

In Table II, some tensile data for the PLLA samples (untreated and treated) are reported. It was observed that the Young's modulus (E) and the stress at break (σ_b) did not change significantly for the samples tested at 60°C, but a significant variation in the strain at break (ϵ_b) was observed. On the other hand, a high decrement in σ_b was observed for the PLLA-2 tested at room temperature because of the lower molecular weight at a high processing temperature. It is important to underline here that despite the decrease in the mechanical properties of PLLA because of the lower molecular weight at high processing conditions, these were always in an acceptable range for some technological applications.

Effect of the molar mass and nucleating agents on the crystallization kinetics of PLLA

Different types of crystalline phases are obtained in relationship to the temperature range where the crystallization of materials occur.^{10,11} On the other hand, it is logical that different processes of crystal growth can occur if the starting phase is glassy or

TABLE II
Effect of the Processing Temperature on the Mechanical Properties of PLLA with Tensile Tests Performed at 25 and 60°C

Sample	Processing temperature (°C)	At 25°C			At 60°C		
		E (MPa)	σ_b (MPa)	ϵ_b (%)	E (MPa)	σ_b (MPa)	ϵ_b (%)
PLLA-1	Untreated	3160 ± 17	64.2 ± 1.8	2.7 ± 0.9	1290 ± 15	21.0 ± 1.3	14.7 ± 2.3
PLLA-2	250	3180 ± 12	33.3 ± 2.7	1.1 ± 1.2	1430 ± 22	19.5 ± 2.2	3.5 ± 1.9
PLLA-3	210	3140 ± 23	65.1 ± 1.5	2.5 ± 0.8	1340 ± 18	20.9 ± 3.2	57.0 ± 1.6

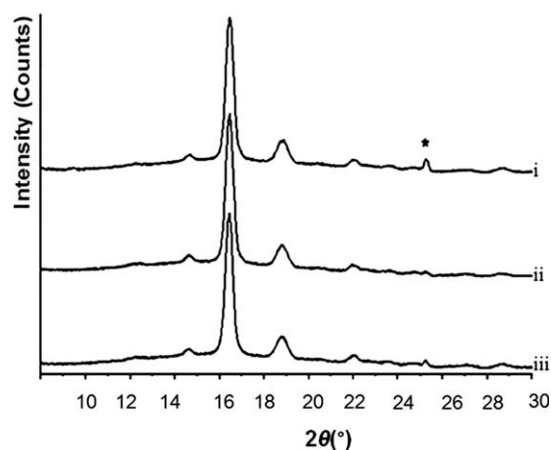


Figure 3 XRD patterns of blends (i) 1, (ii) 2, and (iii) 3 acquired after 30 min at 105°C; the asterisk indicates a Bragg reflection originating from the sample holder (i.e., Al₂O₃).

liquid. Another important consideration is the temperature at which the material should be considered completely fused. In fact, some authors have suggested that some crystalline nuclei should exist in the melt PLLA until a temperature of 230°C. To verify this hypothesis and to gain more insight into the crystallization behavior of blends 1–3, a thermodiffraction study was carried out. Each blend sample was heated in a heating chamber from room temperature to 180°C at a heating rate of 10°C/min in a nitrogen atmosphere, and the spectra were recorded. However, no significant crystalline phases were observed, but the presence of some amount of crystalline nuclei could be expected. The samples were then cooled to isothermal temperature, that is, 105°C, at a cooling rate of –50°C/min, and the spectra were recorded at the beginning and after 30 min at time intervals of 15 min. Different intensities of the crystalline peak were observed for two different isothermal annealing times.

Figure 3 shows the XRD spectra of blends 1–3, acquired after 30 min at 105°C. In this context, it is important to mention that blends 1–3 crystallized at the latter temperature, showing exclusively an orthorhombic morphology (α form).^{36,37} The XRD spectra acquired at 105°C after 15 min differed not significantly from that acquired after 30 min at the same temperature; this confirmed a rapid crystallization of blends 1–3 compared to pure PLLA (Table III).

We decided to perform the kinetic test on melt PLLA at an isothermal temperature of 105°C. This value, in fact, was the middle point of the temperature range between the fusion and the glass transition $(T_m - T_g)/2$, which, in general, should give the highest crystallization rate. However, at this temperature, it was not possible to obtain good crystallization DSC traces after the isothermal process directly

because of a very low crystallization rate observed from some samples (i.e., starting PLLA), and the crystallization peaks were widely distributed in a time range of hours. In light of these results, it was finally decided that the same method would be used for all samples to perform an isothermal step for a defined time and after a fast cooling step (jump) at 25°C; immediately, there was a subsequent heating run at 10°C/min to 200°C. Thus, the same samples underwent various isothermal annealing periods. At the end of the kinetic test, the molar mass of the sample was again controlled, and no appreciable degradation phenomena were observed. This procedure suffered from a few uncertainties because of the presence of crystallization phenomena during the subsequent heating run used to estimate the crystalline phase formed after an isothermal time t . However, there always existed some overlap of the tails of crystallization and fusion peaks, and thus, some errors on the evaluation of crystalline fraction, in particular at the short isothermal time, could have resulted [Fig. 4(a,b)]. The fusion peak showed two overlapped peaks; this was not observed for the sample crystallized at 105°C for 24 h. This suggests that the crystallization process during the dynamic conditions produced a different crystalline form. Some authors suggested the use of modulated DSC for increasing the resolution of the two peaks,^{38,39} but some tests with this analytical methodology gave inconsistent results on the values of the crystallization and fusion enthalpies.

The kinetics of isothermal crystallization was deduced in terms of the Avrami equation⁴⁰ with the double-logarithmic form

$$\ln\{-\ln[1 - X_c(t)]\} = \ln Z + n \ln t \quad (2)$$

where $X_c(t)$ is the crystalline fraction of the material at time t with respect to the total crystallinity at infinite time at isothermal crystallization temperature and n and Z are Avrami crystallization parameters, where n is the Avrami exponent and Z is the global rate constant. $t_{1/2}$ was obtained from the equation $t_{1/2} = [\ln 2/Z]^{1/n}$.

TABLE III
Avrami Isothermal Parameters at 105°C

Sample	n	$-\ln Z$	R^2	$t_{1/2}$ (min) ^a	$t_{1/2}$ (min) ^b
PLLA-1	2.2	10.74	0.992	105	107.7
PLLA-2	3.4	9.45	0.977	15	14.7
PLLA-3	3.0	8.21	0.975	13.5	13.6
Blend 1	3.2	5.83	0.988	5.5	5.5
Blend 2	2.1	5.67	0.929	13.0	13.1
Blend 3	2.5	4.66	0.997	5.5	5.36

^a Experimental value.

^b Value computed from the Avrami parameters.

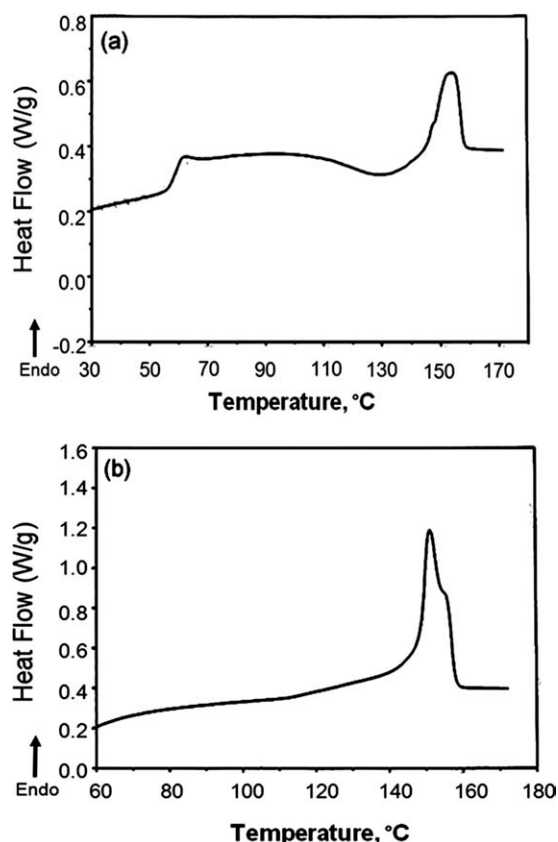


Figure 4 DSC traces obtained after an isothermal annealing period of 30 min at 105°C with a scanning rate of 10°C/min: (a) PLLA-2 and (b) blend 1.

In Table III, the Avrami parameters, evaluated by a two-step method (illustrated previously) with conventional DSC, are summarized. It should be noticed that an acceptable range of different parameters was obtained. In Table III, there is also a comparison between $t_{1/2}$ detected experimentally and that computed with kinetic parameters. Almost analogous values were observed; this indicated that the methods used to study the crystallization kinetics coincided with the purpose of this work.

A dramatic effect of the molecular weight on the crystallization rates was observed. $t_{1/2}$, which is regarded as a very important crystallization kinetic parameter, is usually employed to characterize the crystallization rate directly. It can be said that the longer $t_{1/2}$ was, the slower the crystallization rate was. It was observed in the experiment that when the M_w decreased from 199,000 to 150,000 Da, a decrement of $t_{1/2}$ was observed (Table III); this means that nucleating agents not only had an influence on the decrement of molar mass of PLLA but also increased the crystallization rate. Usually, the rate of crystallization is described as the reciprocal of $t_{1/2}$, that is, $(t_{1/2})^{-1}$. A correlation between the molar mass (M_n) and the crystallization rate is depicted in Figure 5.

Also, the influence of the molar mass decrease was observed by n . n increased from 2.2 to values above 3 (3.4 and 3.0 for PLLA-2 and PLLA-3, respectively). Because the value of n depended on the mechanism of nucleation and on the form of crystal growth, the increase in value of n , thus, could have been an indication of significant variation of the topology of the growth of the crystalline phase. The n values obtained were very close, in the range 2.1–3.4; this implied that the crystals in the PLA/nucleating agent systems showed heterogeneous nucleation and spherulitic growth¹⁸ or a grainlike morphology⁴⁰ (three-dimensional growth that could be confirmed by polarized light microscopy⁴¹) under the experimental conditions. The values of n reported in the literature were in the range 2–5.47,^{14,18} depending on the mechanism of nucleation, the form of crystal growth, and the detection techniques used (e.g., DSC, wide-angle X-ray scattering, Fourier transform infrared spectroscopy). The values here may have been the result of a change of the nucleation mechanism toward a more sporadic nucleation that nuclei generation had greater time dependence⁴² or a thermal nucleation process.⁴³

A significant variation was noticed also in Z , which showed an increase of 1–2 decades. As previously discussed, the addition of 0.3 wt % talc slightly increased the loss in the molar mass, and a higher polydispersity but a significant increase in the crystallization rate were observed as well (Table III, Fig. 6). The observed $t_{1/2}$ decreased from 13.5 (PLLA-3) to 5.5 min (blend 1) could not be explained in a complete way at the light of the decline in molar mass but with a significant nucleation effect. In fact, the sample PLLA-2, having an analogous value of M_w , also showed a $t_{1/2}$ similar to the sample PLLA-3. The exponential parameter n had a value of 3.2, that is, intermediate of those of the samples PLLA-2 and PLLA-3. On the contrary, a dramatic increase in Z was observed, the value of which was about three times higher.

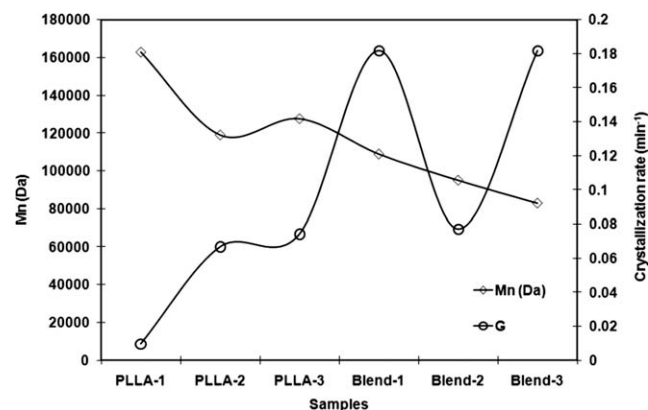


Figure 5 Correlation between the molar mass distribution (M_n) and crystallization rate (G) of samples with and without nucleating agents.

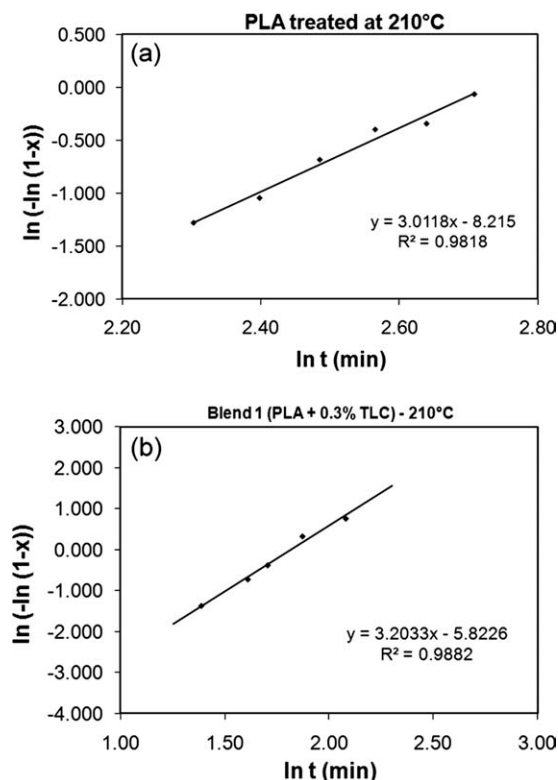


Figure 6 Avrami plot for the PLLA treated at 210°C (a) without nucleants and (b) with 0.3 wt % of talc (blend 1) with isothermal crystallization tests at 105°C. TLC refers to the talc (a nucleating agent used in this work). x represents the crystalline fraction of the material (i.e. PLLA) studied.

So, in fact, the talc-containing sample maintained a high n value and strongly increased the Z constant. On the other hand, the sodium benzoate containing sample did not produce a similar effect on $t_{1/2}$ the value, which was about 13 min. Although the value of Z for the sodium benzoate containing sample was almost similar to that of the material containing talc, the value of n showed a strong decrease with respect to the value of n for talc-containing PLLA ($n = 3.2$ for blend 1 and $n = 2.1$ for blend 2, Table III). However, the value of n for the sodium benzoate containing PLLA was almost similar to that of the starting PLLA ($n = 2.2$ for PLLA-1 and $n = 2.1$ for blend 2, Table III). This indicated a strong effect on the topology of the crystalline phase growth and the influence of molar mass distribution on Z . No synergistic effect was observed when talc and sodium benzoate were added to the matrix, and the material had a $t_{1/2}$ close to that of the sample containing only talc. All of the blends had analogous Z values; this suggested an important effect of molar mass distribution (i.e., a dependence of the number of end groups).

CONCLUSIONS

The crystallization process of PLLA is a very slow and complex process because different crystalline

forms exist and the process rate is dramatically controlled by the molar mass distribution of the polymer. Obviously, the amount of crystalline phases near the equilibrium was controlled by these parameters (i.e., molar mass distribution). In any case, well-controlled processing conditions produced a significant decrease in the molar mass, which enormously increased the rate of the crystallization process; an adequate maintenance of the mechanical properties resulted when a high-molecular-weight PLLA was employed. A significant increment in the crystallization rate was also obtained when a little talc was added as a nucleating agent. However, the mechanical properties were maintained even with a higher decrease in the molar mass of PLLA. On the other hand, the use of sodium benzoate added in small amounts produced a high loss in the molar mass without producing any accelerating effect. With regard to the Avrami parameters, the materials without nucleants showed an increase in both the n and Z parameters. When talc was added, only the value of Z substantially increased.

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