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Nonisothermal Crystallization Kinetics of Poly(lactide)—Effect of Plasticizers and Nucleating Agent

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Poly(lactide), a bio-based aliphatic polyester, is a subject to large research effort. One point of optimization is the acceleration of its crystallization kinetics to promote crystallinity under nonisothermal polymer processing conditions by means of compounding with nucleating agents and plasticizers. The nonisothermal crystallization kinetics of neat and formulated poly(L,D-lactide) (PDLLA) from the melt with talc and polyethylene glycol (PEG) or acetyl tributyl citrate (ATBC) were studied with the help of the Avrami–Jeziorny and Liu–Mo analysis. Talc showed to be a moderately efficient nucleating agent, as it causes only small increase of crystallization kinetics and shows no effect on the crystallization activation energy. A synergistic effect with plasticizers was observed, expanding the crystallization window significantly. PEG was found to be a more efficient plasticizer than ATBC but causes large decrease in the molecular weight average of PDLLA upon thermal treatment. The talc/ATBC system is efficient starting with an ATBC concentration of 9 wt%. The acceleration observed was a crystallization half-time decrease of 30% compared to neat PLA and reaching maximum crystallization enthalpies even at cooling rate of 25°C min⁻¹. The ATBC/talc system can be recommended as an efficient system for acceleration of nonisothermal crystallization kinetics of PDLLA.

INTRODUCTION

Due waste management problem with plastic, wild landfill, and accumulation of plastic debris in marine habitats [1], different environmental sustainable development politics were introduced recently throughout the world. The will to reduce persistent pollution due to the durability and increasing usage of plastics has partially materialized [2]. In this context, considerable efforts have been devoted to develop bio-based substitutes to petroleum-based polymers. In addition to their properties comparable to conventional polymers, bio-based materials have the advantage of using renewable raw materials and some of them have an end-of-life waste management by composting or anaerobic digestion to reduce landfilling [3]. Some of these bio-based polymers are already commercialized. Poly(lactide) (PLA), derived from biomass, is one of the latter. PLA is available in large volume for various applications, such as biomedical application, packaging, electronic housing, textile, automobile interiors, and insulation in building [4–7]. The properties of PLA, such as thermal, mechanical, and barrier, are strongly dependent on the crystallinity degree and crystalline morphology, themselves strongly related to the L/D ratio of the lactic acid units [8–10].

PLA is known for its slow crystallization rate. The crystallization of the homopolymer poly(L,L-lactide) (PLLA) has been extensively studied. In appropriate conditions (crystallization time and temperature) [11] the crystallinity degree of PLLA can reach 45–60% [12, 13]. In isothermal conditions, PLLA crystallizes between 85°C and 150°C with a fastest rate of crystallization in the

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range of 95–115°C [14–16]. In the case of the heteropolymer poly(D,L-lactide) (PDLLA), it has been shown that the crystallinity degree [17] and the crystallization rate [18] decrease with the increase in D-lactic acid content in PLA [10]. In nonisothermal processes, such as injection-molding, the characteristics of PDLLA show a significant drawback to produce samples at high processing rate. One way to improve the crystallization rate of PLA is by formulation, e.g., by adding a nucleating agent that decreases the nucleation activation energy or a plasticizer which increases the mobility of polymer chains.

Diverse types of nucleating agent have been used for PLA such as clay, organic or inorganic compounds, talc or D-lactic acid to form stereocomplexes in order to improve the isothermal crystallization of PLA. The stereocomplexes of PLLA/poly(D-lactic acid) (PDLA) are very efficient nucleating agent due to self-nucleation [19]. For example, Schmidt et al. [19], who tested a series of different inclusion percentages of PDLA in a self-synthesized PLLA, showed that at the most efficient inclusion percentage 15 wt% the half time of crystallization ($t_{1/2}$) at 140°C decreased from 44.7 min for neat PLLA to 1.31 min. A paper by Anderson et al. [20] on commercial PLLA grade also showed the high efficiency of PDLA, in which addition of 3% decreased the $t_{1/2}$ from 17 min to less than 1 min at 140°C. Organic compounds, such as *N,N*-ethylen-bis-12-hydroxystereamide or molecules having hydrazide end groups, can increase the nucleating density and crystallization rate of PDLLA [21, 22]. Clays, which are used for reinforcement and improvement of the barrier properties, have been evaluated as nucleating agent. Nam et al. [23] showed an increase in the spherulites diameter and the overall crystallization rate, whereas reduced crystallization ability was noticed by Pluta [24] with organically modified montmorillonites. Talc, a very conventional filler, is a good candidate. It showed a $t_{1/2}$ measured at 140°C from 44.7 to 19 min with 6% of talc in self-synthesized PLLA [19], and from 17 to 6.5 min of a commercial grade [20]. The ability of talc to further the crystallization of PDLLA has been highlighted by Harris and Lee [21] who measured at 115°C a $t_{1/2}$ of 38.2 min without and 0.6 min with 2% of talc, respectively. As previously mentioned the addition of plasticizer may increase the mobility of segment polymers, thus increasing the crystallization rate of PLA. Various plasticizers have already been tested with PLA in order to diminish its brittleness, such as glycerol and oligomeric lactic acid [25], triacetate [26], triphenyl phosphate (TPP) [27], polyadipates [28, 29], poly(propylene glycol) (PPG) [30, 31], poly(ethylene glycol) (PEG) [25, 31–35], and acetyl tributyl citrate (ATBC) [26, 32, 35–37]. However few of them have been added to modify the crystallization rate of PDLLA. As shown by Piorkowska et al. [38] and Kulinski et al. [31] the addition of PPG (425 and 1000 g.mol⁻¹) PEG (600 g.mol⁻¹) induces a significant increase in the crystal growth rate where PEG is more efficient. A content of 12.5 wt% PEG in PDLLA leads to a

multiplication of the crystal growth rate by 24. Therefore spherulites of 10 μm radius were formed after 15 min at 90°C. Li and Huneault [18] tested the effects of PEG (3350 g.mol⁻¹) and acetyl triethyl citrate on PDLLA at 20°C.min⁻¹. It turned out that the addition of PEG induced crystallization upon cooling and a large shift of the crystallization temperature to lower temperature. Triphenyl phosphate (TPP) has also been tested on PDLLA with good results. Xiao et al. [27, 39] showed that, upon isothermal crystallization, the crystal growth rate optimum is tripled and shifted to lower temperature thanks to the introduction of 20% of TPP in PDLLA. The crystallization rate constant and $t_{1/2}$ decreased with the increase in TPP content.

The synergistic effect of nucleating agent and plasticizer has been rarely studied till date, though. Xiao et al. [40] noticed that the addition of talc to the plasticized PLA increased the crystallization rate constant if it was compared to neat PLA but decreased if compared to the rate constant of plasticized PLA. On the contrary, Li and Huneault [18] showed that the addition of PEG to PDLLA/talc decreased $t_{1/2}$ and increased the crystallization peak temperature at various cooling rates.

In conclusion, plasticizing of PDLLA has already received large attention, but most of the studies were focused on the effect on thermal and mechanical properties. Studies investigating the crystallization kinetics of such systems are far less numerous and the investigation of nonisothermal crystallization kinetics of PDLLA, although important for the injection-molding process, has been subject only to a few publications. Among PLA formulations studied, the most promising system seems to be talc as nucleating agent and citrate derivatives as plasticizer. PEG is also very efficient, but has the drawback of inducing polymer degradation during processing [35, 41, 42].

The aim of this study is to investigate and provide data on the effect of nucleating agent and plasticizer on the nonisothermal crystallization kinetics of PDLLA. The nucleating ability of talc and the efficiency of one citrate derivatives, ATBC, to speed PDLLA crystallization were investigated in comparison with PEG. Two models, i.e., the Avrami–Jeziorny and Liu–Mo model, were used to assess the influence of the plasticizer and the nucleating agent on the PDLLA crystallization. The activation energies of neat and formulated PDLLA were also estimated by the Kissinger method.

EXPERIMENTAL SECTION

Materials

The PDLLA pellets were provided by NatureWorks. The content of L-lactide was about 92 wt%. The average molecular weight was 9.0×10^4 g.mol⁻¹ with a polydispersity index of 2.75.

ATBC and PEG, used as plasticizers, were purchased from Sigma Aldrich (France). The molecular weight of ATBC and PEG are $402 \text{ g}\cdot\text{mol}^{-1}$ and around $300 \text{ g}\cdot\text{mol}^{-1}$, respectively. Talc, with a median diameter of $13.5 \mu\text{m}$, is used as a nucleating agent (RioTinto, Luzenac, France).

Sample Preparation

PLA pellets, plasticizer, and nucleating agent were dried at 80°C overnight in a vacuum oven. PLA and additives were introduced in the feeding zone of an internal mixer (Counter rotating mixer Rheocord 9000, Haake, USA) at 160°C to melt PLA pellets and mix at 60 rpm for 15 min. The ATBC or PEG content varied between 4 wt% and 17 wt% of PLA. Talc was added at 1, 2 or 5 wt% of PLA. The neat PLA sample was also processed in the thermal mixer for comparison reasons.

After drying all the formulated materials during 4 h at 80°C , the different PLA formulations were thermo-compressed at 185°C and 150 bar. The films of approximately $150 \mu\text{m}$ thickness were then quenched at ambient temperature. Amorphous films were stored at ambient temperature in a desiccator over P_2O_5 .

Size Exclusion Chromatography

The average molecular weight and the dispersity index were measured by Size Exclusion Chromatography (SEC) using a Shimadzu apparatus equipped with an RID-10A refractive index detector and an SPD-M10A UV detector. The analyses were carried out at 30°C and $0.8 \text{ mL}\cdot\text{min}^{-1}$ in chloroform on a PLgel $5 \mu\text{m}$ Guard column and two PL Gel $5 \mu\text{m}$ Mixed-C columns. The calibration was performed with polystyrene standards from 580 to $1,650,000 \text{ g}\cdot\text{mol}^{-1}$.

Thermal Analysis

The thermal characterization and the crystallization studied were performed with a differential scanning calorimeter (DSC Q100, TA Instruments) under nitrogen atmosphere (flow rate $50 \text{ mL}\cdot\text{min}^{-1}$). The apparatus, equipped of a refrigerated cooling system (TA Instruments), is calibrated with indium as standard. The samples (about 10 mg) were put into hermetic aluminum pans (TZero, TA Instruments). The nonisothermal crystallization kinetic experiments were carried in two steps. The samples were heated to 190°C at $10^\circ\text{C}\cdot\text{min}^{-1}$ and maintained at this temperature for 5 min to erase any thermal history. Then all the formulated PLA were cooled down to -30°C to study the nonisothermal crystallization from the melt. The different cooling rates are: 2, 5, 10, 15, 20, or $25^\circ\text{C}\cdot\text{min}^{-1}$. From the curves, the peak temperature of the crystallization (T_p), the peak enthalpy (ΔH_c), and the span of the peak ($T_{0.99}-T_{0.01}$) were obtained. The temperatures $T_{0.01}$ and $T_{0.99}$ are the temperatures at which the relative degree of crystallinity amounts to 1% and 99%, respectively.

RESULTS AND DISCUSSION

Nonisothermal Crystallization Behavior

The crystallization exotherms from the melt in nonisothermal conditions of typical formulations of PDLLA are plotted in Fig. 1 and the corresponding enthalpies of crystallization (ΔH_c) are given in Table 1.

We considered crystallization enthalpies below $5 \text{ J}\cdot\text{g}^{-1}$ to be nonsignificant, because they were on the detection limit of our DSC equipment and the value in this case was dependent on placing of the baseline. The neat PLA showed no significant crystallization (Table 1) under the chosen measurement conditions. The addition of talc, a widely used nucleating agent of PDLLA, leads to a slight increase in the crystallization enthalpy but the peak is still invisible on Fig. 1. Significant crystallization is obtained at 5% talc for a similar cooling rate, suggesting the need for a certain quantity of nuclei before efficient promotion of the crystallinity (Table 1). In comparison, Xiao et al. [43], obtained a crystallization enthalpy of $29.6 \text{ J}\cdot\text{g}^{-1}$ upon addition of 1.2% talc in neat PDLLA and Li et al. [44] obtained $29.04 \text{ J}\cdot\text{g}^{-1}$ with 1% of talc. One of the reasons might be the different D-lactic acid content in the samples. PDLLA with higher D-lactic acid content crystallizes more slowly [10]. The samples of Xiao et al. [43] and Li et al. [44] contained approximately 2% D-lactic acid, compared to approximately 8% D-lactic acid for our samples. Furthermore, increasing the talc content increases the crystallization peak temperature and decreases the width of the peak of 10°C (Table 1). It clearly shows that talc can promote the crystallization, with enlarging the crystallization window in the higher temperature range due to efficient nucleation. To facilitate the mobility of PDLLA chains and further promote crystallization, the plasticizers ATBC and PEG were used. The plasticization of PDLLA by PEG induces an increase in the crystallization enthalpy, and decreases the width of the peak (Fig. 1). At PEG contents higher than 5 wt% a maximum crystallization enthalpy seems to be reached (Table 1). Therefore this plasticizer furthers the

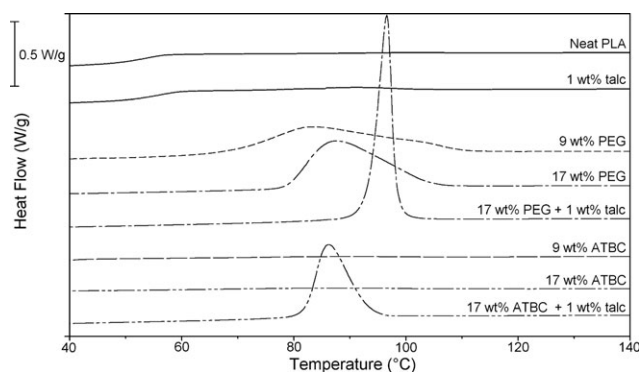


FIG. 1. DSC thermograms for neat PDLLA and formulated PLA cooled at $10^\circ\text{C}\cdot\text{min}^{-1}$. Exotherms are up.

TABLE 1. Peak temperature (T_p), peak width ($T_{0.01}-T_{0.99}$), crystallization half time ($t_{1/2}$), crystallization enthalpy (ΔH_c), Avrami exponents in the first and second crystallization regime (n_{a1} , n_{a2}), Avrami crystallization rate constants (k_a), and Avrami-Jeziorny rate constants (k_c) in the first and second crystallization regime of neat PDLLA, PDLLA with various talc content and formulated PDLLA with plasticizer and talc recorded at $10^\circ\text{C}\cdot\text{min}^{-1}$ cooling rate.

Samples	Plasticizer content (wt%)	Tp (°C)	$T_{0.01}-T_{0.99}$ (°C)	$t_{1/2}$ (min)	ΔH_c ($\text{J}\cdot\text{g}^{-1}$)	Primary crystallization ($5 < X(t) < 97\%$)				Secondary crystallization ($97 < X(t) < 99.9\%$)			
						n_{a1}	$k_{a1} \times 10^3$ (min^{-n})	$k_{c1} \times 10^3$ (min^{-n})	$t_{1/2,c1}$ (min)	n_{a2}	$k_{a2} \times 10^3$ (min^{-n})	$k_{c2} \times 10^3$ (min^{-n})	$t_{1/2,c2}$ (min)
Neat PDLLA	-	98.8 ± 4.4	28.4 ± 6.7	-	0.4 ± 0.3	-	-	-	-	-	-	-	-
PDLLA /1 wt% talc	-	90.8 ± 2.6	29.6 ± 4.0	2.1 ± 0.3	4.9 ± 2.5	-	-	-	-	-	-	-	-
PDLLA /2 wt% talc	-	89.5 ± 0.1	34.5 ± 0.5	2.0 ± 0.2	8.2 ± 0.1	3.3 ± 0.5	67 ± 38	757 ± 45	0.97 ± 0.02	2.8 ± 0.3	93 ± 23	788 ± 19	0.95 ± 0.01
PDLLA /5 wt% talc	-	95.6 ± 0.1	24.5 ± 1.8	1.7 ± 0.4	29.4 ± 0.6	4.4 ± 0.9	22 ± 6	743 ± 106	0.98 ± 0.04	2.8 ± 0.1	202 ± 57	850 ± 23	0.93 ± 0.01
PDLLA /PEG	5	79.9 ± 0.8	39.5 ± 4.3	2.2 ± 0.2	5.1 ± 3.5	2.8 ± 0.2	71 ± 26	764 ± 30	0.97 ± 0.02	3.8 ± 0.5	19 ± 8	667 ± 30	1.01 ± 0.01
	9	84.5 ± 2.0	44.7 ± 3.5	2.9 ± 0.3	33.5 ± 2.8	3.6 ± 0.4	15 ± 5	654 ± 23	1.00 ± 0.01	3.1 ± 0.2	26 ± 9	693 ± 24	1.00 ± 0.01
	13	82.2 ± 0.2	29.9 ± 0.6	2.7 ± 0.1	34.8 ± 0.6	3.4 ± 0.2	26 ± 7	694 ± 19	1.00 ± 0.01	2.6 ± 0.3	135 ± 59	877 ± 110	0.94 ± 0.02
	17	83.8 ± 6.8	28.5 ± 4.1	2.3 ± 0.1	32.1 ± 3.9	3.7 ± 0.3	35 ± 5	715 ± 9	0.99 ± 0.01	2.8 ± 0.2	131 ± 62	858 ± 100	0.95 ± 0.02
PDLLA /1 wt% talc /PEG	5	93.6 ± 0.5	17.0 ± 1.0	1.3 ± 0.1	32.2 ± 0.4	4.3 ± 0.3	233 ± 66	862 ± 26	0.95 ± 0.01	1.9 ± 0.5	1101 ± 271	1008 ± 25	0.81 ± 0.06
	9	100.3 ± 1.3	10.8 ± 0.4	1.0 ± 0.1	34.5 ± 1.4	7.2 ± 1.0	661 ± 313	953 ± 44	0.96 ± 0.01	1.9 ± 0.4	1874 ± 397	1064 ± 22	0.79 ± 0.05
	13	98.3 ± 0.1	17.9 ± 4.0	1.7 ± 0.4	35.3 ± 0.6	9.9 ± 1.3	234 ± 38	592 ± 162	1.02 ± 0.03	2.0 ± 0.4	848 ± 134	983 ± 15	0.84 ± 0.02
	17	95.8 ± 5.3	13.0 ± 3.0	1.1 ± 0.1	31.5 ± 3.5	7.8 ± 1.0	291 ± 206	871 ± 58	0.37 ± 0.01	1.6 ± 0.4	1666 ± 373	1051 ± 22	0.77 ± 0.06
PDLLA /ATBC	4	87.6 ± 7.4	38.3 ± 2.4	-	0.2 ± 0.1	-	-	-	-	-	-	-	-
	9	85.9 ± 1.8	44.7 ± 1.0	-	1.5 ± 0.2	-	-	-	-	-	-	-	-
	13	89.5 ± 6.5	52.2 ± 3.0	-	3.3 ± 0.6	-	-	-	-	-	-	-	-
	17	78.9 ± 1.7	53.4 ± 2.2	-	3.2 ± 2.0	-	-	-	-	-	-	-	-
PDLLA /1 wt% talc /ATBC	4	85.6 ± 0.1	35.3 ± 0.4	1.8 ± 0.1	11.7 ± 3.7	3.6 ± 0.2	35 ± 12	713 ± 22	0.94 ± 0.01	2.4 ± 0.1	119 ± 8	808 ± 5	0.96 ± 0.02
	9	91.2 ± 0.4	17.1 ± 0.9	1.5 ± 0.1	29.4 ± 0.3	7.7 ± 0.8	14 ± 7	647 ± 35	0.98 ± 0.01	2.1 ± 0.2	840 ± 146	979 ± 24	0.81 ± 0.03
	13	91.8 ± 1.8	14.8 ± 1.8	1.3 ± 0.2	27.8 ± 1.5	6.9 ± 0.9	47 ± 10	736 ± 156	0.96 ± 0.02	2.3 ± 0.3	575 ± 265	966 ± 21	0.85 ± 0.05
	17	87.6 ± 2.4	14.8 ± 1.6	1.3 ± 0.2	25.1 ± 1.7	8.1 ± 0.2	77 ± 13	774 ± 13	0.95 ± 0.01	1.8 ± 0.4	1456 ± 318	1037 ± 24	0.79 ± 0.07

crystallization of PLA upon cooling by enhancing the polymer mobility. This is more noticeable in the lower temperature window, which causes the peak temperature to shift down. ATBC, in contrary, showed less efficiency in promoting crystallization. Even at 17 wt% of ATBC no significant peaks were obtained (Fig. 1 and Table 1).

The combination of both additives, plasticizer and nucleating agent, had the expected synergistic effect. In the case of PEG/talc, high crystallinity degrees were obtained (Table 1 and Fig. 1). The peaks were comparatively thinner and shifted to higher temperatures. In the case of ATBC/talc, significant crystallization could be obtained for each formulation. For ATBC contents higher than 5 wt%, a maximum crystallization enthalpy degree was reached (Table 1). The difference between both systems clearly shows that PEG is a more efficient plasticizer for PDLLA than ATBC. Those results are qualitatively in agreement with the results of Li et al. [44], based on PEG with a molecular weight of 6000.

The relative crystallinity degree (χ), as a function of temperature (T), was calculated from the energy released over the nonisothermal crystallization process. It can be defined by the Eq. 1 where T_0 and T_∞ represent the onset and end of crystallization temperature, respectively, and dH_c is the measured enthalpy of crystallization for an infinitesimal temperature range dT :

$$\chi(T) = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT}, \quad (1)$$

If we consider that the difference temperature between the sample and the DSC furnace is negligible, the relative crystallinity degree as a function of time can be obtained from Eq. 2, where α is the cooling rate and t represents time,

$$t = \frac{T_0 - T}{\alpha}. \quad (2)$$

The relative crystallinity is represented as a function of time in Fig. 2 for the formulations of PDLLA where crystallization enthalpies higher than 5 J.g⁻¹ were observed. All the curves present a sigmoidal profile with a linear trend between 0.2 and 0.8 of relative crystallinity. One important parameter to take from this plot is the half time ($t_{1/2}$) of crystallization, which is defined by the time from the onset to the time at which $\chi(t)$ equals 50%. The $t_{1/2}$ is given in Table 1. The addition of talc seemed to lower the crystallization half time, but the effect observed was not significant with regards to the experimental error. Literature results for comparison are given in Table 2. The observed $t_{1/2}$ were smaller, which can be explained by the difference in PLA D-lactic acid content. Li et al. [44] show furthermore even an increase in $t_{1/2}$ in the case of addition of talc, which might be explained by the low signal observed in the case of the neat PLA. Addition of plasticizer PEG alone seemed also to be slow down reac-

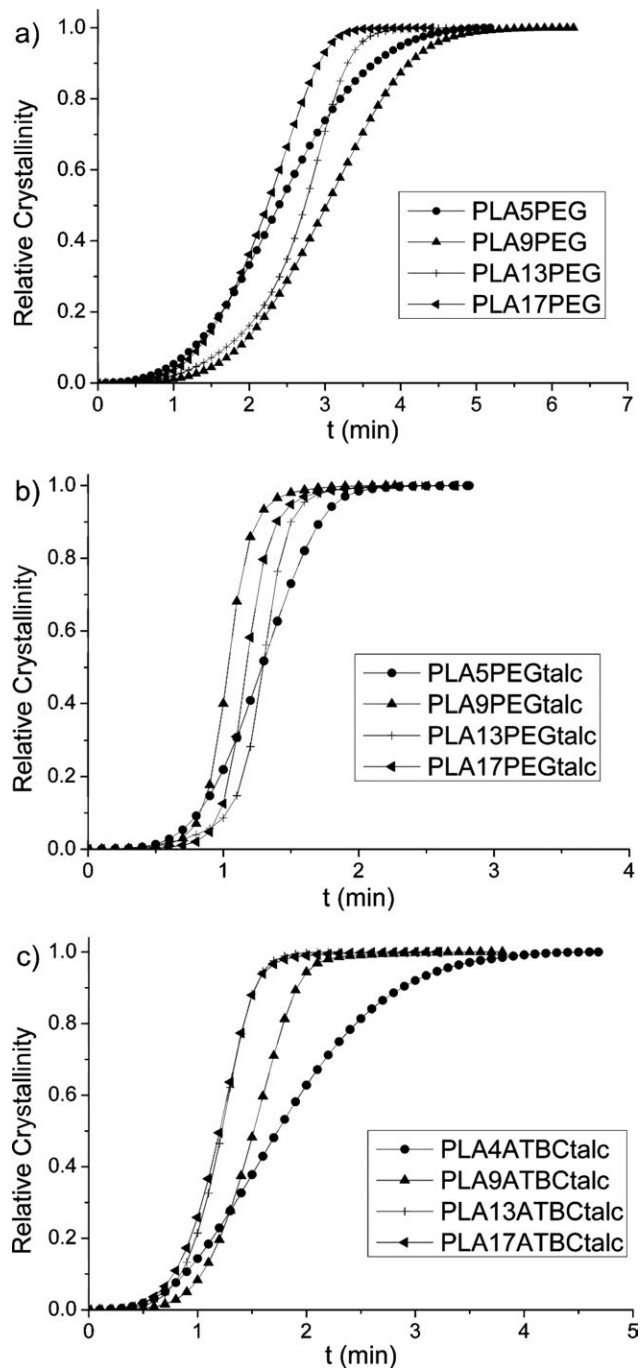


FIG. 2. Variation of relative crystallinity versus crystallization time for (a) PDLLA/ different percentages PEG, (b) PDLLA /1 wt% talc/ different percentages PEG, and (c) PDLLA/1 wt% talc/different percentages ATBC for nonisothermal crystallization at 10°C.min⁻¹.

tion rate, and $t_{1/2}$ grew larger (Table 1). The simultaneous presence of plasticizer and nucleating agent made it possible to decrease the $t_{1/2}$ for the PEG/talc system and to measure significant crystallization enthalpies for the ATBC/ talc system. This shows the synergistic effects between both compounds.

An important drawback of the PEG system is however, as shown in Table 3, the strong decrease in the molecular weight of the plasticized samples. The ability of PEG to

TABLE 2. Literature data on half times and modified Avrami–Jeziorny parameters of different PLA grades at a cooling rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

	D-LA ^a (%)	talc [%]	$t_{1/2}$ (min)	n_a	K_c (min^{-n})	$t_{1/2,a}$ (min) ^b	Ref.
PDLLA	2	0	1.42	2.1	0.317	1.45	[44]
		1	1.56	3.9	0.115	1.59	
PDLLA/PEG 5%		1	1.08	4.1	0.493	1.09	
PDLLA/PEG 10%		1	0.96	4.6	0.883	0.95	
PDLLA/PEG 20%		1	0.78	4.7	2.228	0.78	
PDLLA	2 [18]	0		2.6	0.842	0.93	[43]
PDLLA regime 1 ^c		1.2		3.9	0.254	1.29	
PDLLA regime 2 ^c		1.2		2.5	0.423	1.22	
PDLLA/ TPP ^d 15% regime 1		1.2		4.6	0.211	1.30	
PDLLA/ TPP ^d 15% regime 2		1.2		2.2	0.500	1.16	
PDLLA	3.3	0	1.42	2.1	0.685	1.01	[58]
PLLA	0	0		1.3	0.75	0.94	[17]

^a Molar percentage of D-lactic acid.

^b Values calculated by Eq. 6 from literature data.

^c Regime 1 and 2 after nomenclature of our article match regime 2 and 3 of Xiao et al. [43].

^d Triphenyl phosphate.

degrade PLA has been already described for hydroxyl containing additives, one of the main mechanism could be polymer chain scission by transesterification [41, 42]. On one hand, this degradation may increase the nucleation and so further the crystallization, but on the other hand this mechanism imparts the rheological and mechanical properties of the polymer and is generally unwanted. Furthermore, exudation of PEG occurs at plasticizer contents higher than 9%, which was evidenced for PEG 300 by Courgneau et al. [35] The decrease of molecular weight is less important, when PDLLA is plasticized with ATBC, which led us to conclude, that even if PEG was more efficient than ATBC in yielding high crystallization enthalpies, the latter might be a better compromise for maintaining final product properties.

Modified Avrami–Jeziorny Analysis of Nonisothermal Crystallization Kinetics

To go further in the analysis of the crystallization kinetics and allow comparison to literature data, different approaches were carried out on the analysis of the DSC signal. The most common approach used to describe the overall isothermal crystallization is the Avrami equation [45–47] given by Eq. 3 where k_a and n_a are the Avrami crystallization rate and exponent, respectively.

$$\chi(t) = 1 - \exp(-k_a t^{n_a}) \in [0, 1], \quad (3)$$

The parameter n_a depends on the nucleation type (homogeneous or heterogeneous) and growth process parameters (rod, disc, sphere, and sheaf) [48].

Equation 3 can be transformed into Eq. 4, by taking the double logarithmic form.

$$\log(-\ln(1 - \chi(t))) = \log k_a + n_a \log t, \quad (4)$$

Considering the nonisothermal character of the process, Jeziorny [49] suggested to correct the value of k_a by tak-

ing into account the cooling rate of the experiment (α), as shown in Eq. 5:

$$\log k_c = \frac{\log k_a}{\alpha}. \quad (5)$$

The n_a and k_a values have been determined upon cooling at $10^\circ\text{C}\cdot\text{min}^{-1}$ thanks to the plots of $\log(\ln(1 - \chi(t)))$ versus $\log t$ and then gathered in Table 1. Raw data are plotted in Fig. 3. With the help of the fitted Avrami–Jeziorny parameters the half time of crystallization ($t_{1/2,a}$) was calculated according to Eq. 6 [50]:

$$t_{1/2,c} = \left(\frac{\ln 2}{k_c} \right)^{1/n_a}. \quad (6)$$

 TABLE 3. Number and weight average molecular weight (M_n and M_w) of neat and formulated PDLLA.

Samples	Plasticizer content (wt%)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)
Neat PDLLA ^a	–	66,700	158,000
PDLLA / 1 wt% talc	–	50,850	137,750
PDLLA / 2 wt% talc	–	88,100	226,450
PDLLA / 5 wt% talc	–	54,450	122,400
PDLLA / PEG ^a	5	55,850	155,850
	9	31,300	68,000
	13	36,350	66,850
	17	27,500	49,950
PDLLA / 1 wt% talc / PEG	5	51,100	141,550
	9	26,500	50,700
	13	31,800	61,650
	17	27,200	49,600
PDLLA / ATBC ^a	4	98,900	228,100
	9	59,100	143,650
	13	57,550	123,900
	17	55,050	133,950
PDLLA / 1 wt% talc / ATBC	4	91,400	227,350
	9	59,900	149,250
	13	48,550	102,800
	17	51,350	117,450

^a Data already published [35].

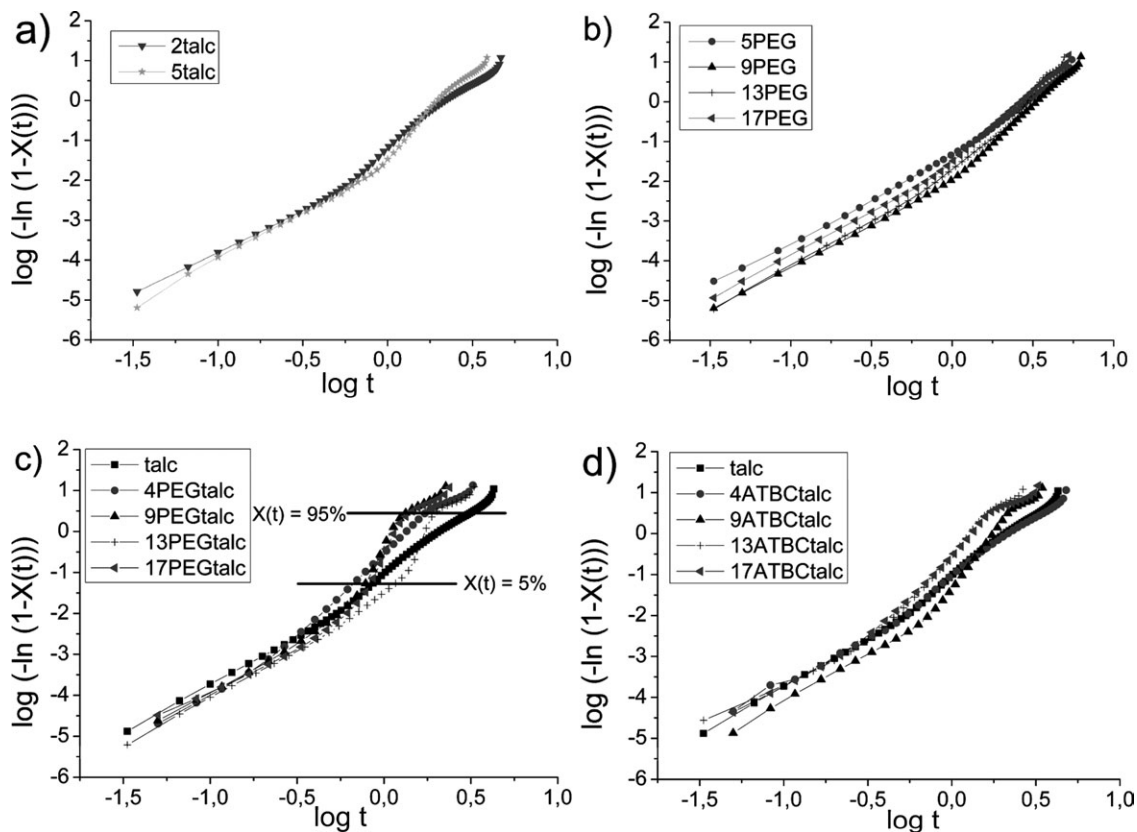


FIG. 3. Plots of $\log(-\ln(1-X(t)))$ versus $\log t$ for nonisothermal crystallization at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ of (a) PDLLA/ different percentages talc, (b) PDLLA/ different percentages PEG, (c) PDLLA/ 1 wt% talc/ different percentages PEG, and (d) PDLLA/ 1 wt% talc/ different percentages ATBC.

Different shapes of the curves after the Avrami–Jeziorny linearization can be distinguished depending on the formulation of PDLLA (Fig. 3). All curves present three different linear regimes: before 5% of relative crystallinity (regime 1), between 5% and 97% (regime 2) and after 97% (regime 3). Vertical bars were added in Fig. 3 to show the borders of the different regimes were taken. The PEG plasticized PDLLA samples present flat curves whereas the addition of talc results in marked transition between the different regimes (Fig. 3). According to Xiao et al. [43] regime 1 and 2 correspond to the primary crystallization of PDLLA while regime 3 is due to the secondary crystallization of PLA.

Although fit parameters of the modified Avrami–Jeziorny analysis have only marginal intrinsic value, their analysis is useful for comparison reasons in the aim of optimizing plasticizer/nucleating agent systems for PLA. The modified Avrami–Jeziorny parameters obtained the main crystallization regimes (2 and 3), corresponding to primary and secondary crystallization which were analyzed and are given in Table 1. Table 2 shows a summary of literature data, in order to facilitate comparison between studies. Although modified Avrami–Jeziorny values are given in literature, even in the case of for very small crystallization enthalpies, we choose not to analyze experiments where the total crystallization enthalpy was

lower than $5 \text{ J}\cdot\text{g}^{-1}$, because such small signals were on the detection limit of our DSC equipment.

The analysis of the Avrami–Jeziorny parameters for our samples showed that systems with talc had higher n_{a1} values compared to neat PDLLA literature values (Table 2) and that n_{a1} increased with increasing talc content. No modification in k_c was observed in our formulations (Table 1). The n_{a2} values of the PDLLA/talc samples were smaller than the n_{a1} values for the higher talc concentrations, which was also observed by Li et al. [44] (Table 2). Comparing the plasticized samples, only the formulations containing PEG crystallized significantly at the cooling rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$. Starting from 9 wt% of PEG, n_{a1} reached a value of ca. 3.5 which did not vary with the plasticizer content. Li et al. showed in the case of PEG 6000 a still higher n_a of 4 and higher k_{a1} values, which might point to even more efficiency of a PEG with higher molecular weight. Table 1 shows furthermore that the n_{a2} value decreased slightly compared to n_{a1} . Xiao et al. [43] noticed a similar behavior for the PDLLA/TPP system.

The simultaneous presence of talc and PEG in PDLLA lead in regime 2 to a large increase in the average n_a value up to 8 (Fig. 3c and Table 1). Such n_a values were retrieved by Liu et al. [51] and Balamurugan and Maiti [48] with polyamide 6. It suggests that the

nucleation and growth geometry is complex. As explained by Balamurugan and Maiti [48], $n_a > 4$ may be due to an increasing rate of nucleation, implying simultaneous appearance of different growth mechanisms, which are no longer constant throughout the crystallization process. However, Zhang et al. [52] showed that even for simulated data, the modified Avrami–Jeziorny analysis yields n_a values as high as 9. Therefore the parameters should be viewed as fitting constants rather than physical parameters. The constants retrieved for the PEG/talc system showed high experimental uncertainty. We suppose that this uncertainty was caused by the exudation of PEG from the PDLLA/PEG films. This phenomenon has been previously described by Courgneau et al. for the same type of samples [35]. The PDLLA/ATBC/talc system seemed to be more stable, although primary crystallization was slower compared to the PDLLA/PEG/talc sample. Compared to the results of Xiao et al. [43] (Table 2), it appeared that the addition of ATBC and talc resulted in a faster crystallization kinetics of PDLLA than TPP/talc system. Moreover, as shown by Xiao et al. [43], the simultaneous presence of nucleating agent and plasticizer induced a significant increase in n_a values in regime 2 while causing decrease in regime 3.

Consequently whatever the plasticizer, the addition of talc and plasticizer to PLA results in a complex crystallization and it is interesting to calculate half times of the different crystallization regimes which can be detected with the help of the modified Avrami–Jeziorny data analysis, in the aim to get more insight into growth kinetics. The half time on the high temperature side, $t_{1/2,a1}$, did not show changes when PLA was formulated. In particular, addition of talc did not seem to have an effect. This would lead to conclude that talc is not efficient enough to introduce a nucleating effect under the chosen experimental conditions. On the low temperature side of the crystallization peak, $t_{1/2,a2}$ showed a slight decrease when plasticizer was added. The comparison between the PEG and the ATBC system showed that PEG seemed to be more efficient, but with more heterogeneity. Compared to the TPP system studied by Xiao et al. [43] (Table 2), both present systems showed slightly lower half times.

Nonisothermal Crystallization Kinetics of PDLLA/ATBC/Talc at Various Cooling Rates

Considering the plasticizer exudation at high content of PEG in PDLLA [35] and a large decrease in molecular weight of PDLLA (Table 3), the system of ATBC/talc seemed to be a better compromise for enhancing PDLLA crystallization kinetics. To investigate the crystallization kinetics the nonisothermal crystallization of PDLLA/ATBC/talc was studied at different cooling rates through different models.

Figure 4 shows the DSC thermograms of nonisothermal crystallization of neat and formulated PDLLA at various cooling rates. Neat PDLLA presented a broad peak at

$2^\circ\text{C}\cdot\text{min}^{-1}$ which shifted to lower temperature with the increase in cooling rate and at cooling rates higher than $5^\circ\text{C}\cdot\text{min}^{-1}$ no signal was observed any more. Upon addition of 1 wt% talc, crystallization could still be observed at a cooling rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. Crystallization enthalpy was measured at cooling rates up to $25^\circ\text{C}\cdot\text{min}^{-1}$ for PDLLA with talc and ATBC (Table 4), confirming the acceleration of the crystallization kinetics upon formulation. Interestingly, at the intermediate ATBC contents (4, 9, and 13 wt%) the peaks observed at 2 and $5^\circ\text{C}\cdot\text{min}^{-1}$ seemed to have a different behavior. Shape is thinner and there was a shoulder at the right of the crystallization peak for PDLLA formulated with talc and ATBC.

Modified Avrami–Jeziorny Analysis

Figure 5 presents the plots of $\log(-\ln(1 - X(t)))$ versus $\log t$ from which n_a and k_a parameters were obtained. The corresponding values are given in Table 4. The n_{a1} of the neat sample was 2.9 and the n_{a2} was 3.0. Formulation of the neat PDLLA increased the n_{a1} and diminished the n_{a2} , as was already observed in Table 1. Among formulated PDLLA/ATBC/talc samples the n_{a2} remained approximately constant, with an overall average value of 2. As expected, both rate constants, k_{c1} and k_{c2} , accelerated with increasing cooling ramp.

At the primary crystallization regime which corresponds to the fast crystal growth of PDLLA in the higher temperature range, n_{a1} values spread between 3.0 and 11 for all the formulated PDLLA. The value of the Avrami exponent 11 is impossible to be reached in the original work of Avrami for isothermal crystallization. As already mentioned earlier, the parameters of the modified Avrami–Jeziorny analysis are fitting parameters and do not hold physical meaning but allow for the calculation of the half times observed at the low and high temperature side of the crystallization peak (Table 4). The half times of the process at the high temperature side ($t_{1/2,a1}$) show at $2^\circ\text{C}\cdot\text{min}^{-1}$ that the addition of talc brought about a small gain in the kinetics due to the nucleating effect. Talc could be considered as a moderately efficient nucleating agent in the present system. Looking on the low temperature side, $t_{1/2,a1}$, one can observe that up to a cooling rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ ATBC seems not to have influence on the crystallization rate supplementary to the gain stemming from the talc addition. To obtain crystallization at higher cooling rates the adding of the plasticizer was required, though. Among formulations with different ATBC concentrations, no significant differences of half times of both processes were found for contents equal to or higher than 9 wt%. As a conclusion, ATBC is an efficient plasticizer for PLA under the condition that it is used in synergy with a nucleating agent.

Liu and Mo Analysis

To go further in the kinetic analysis of the present data set, different models published for the analysis of

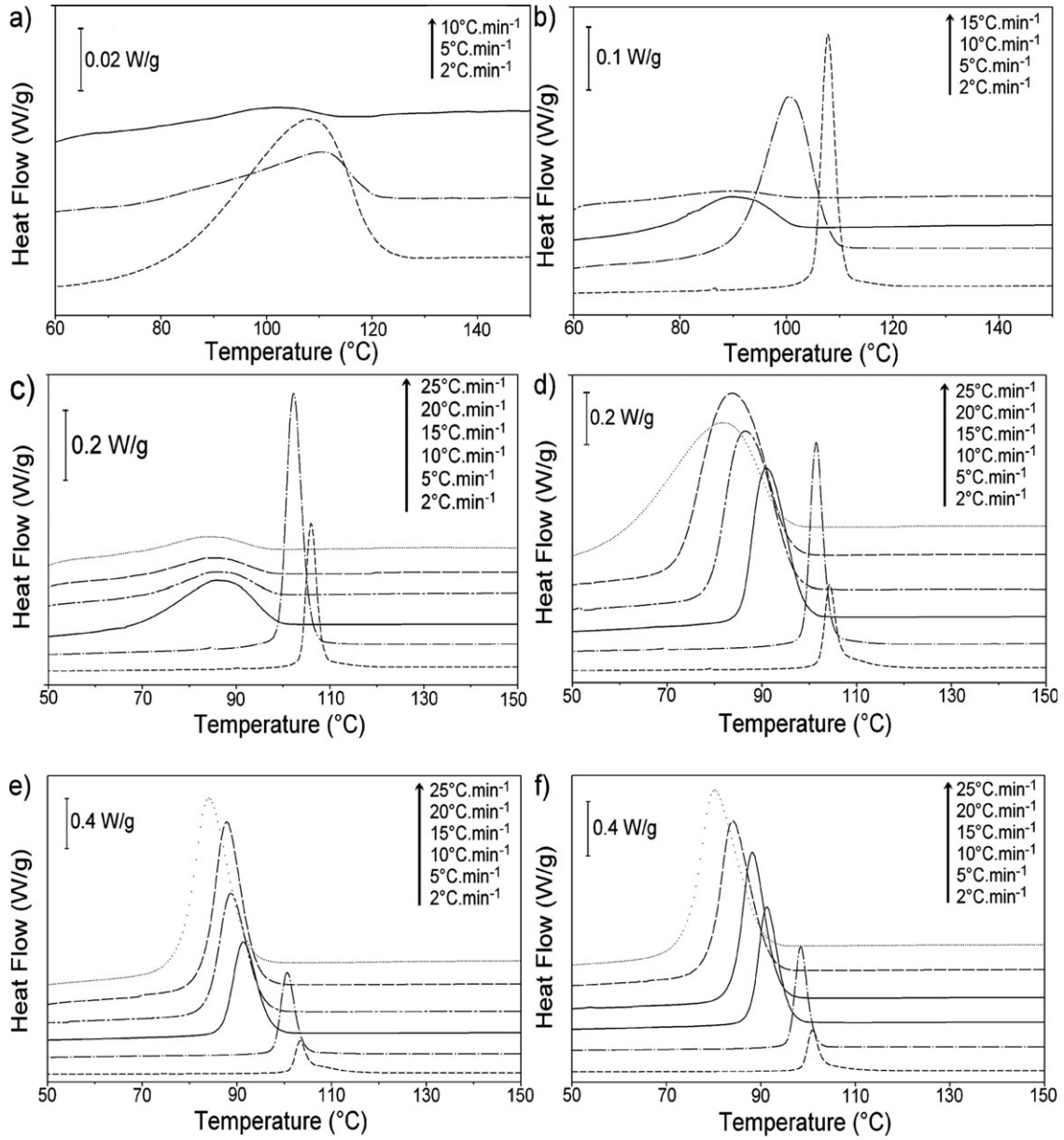


FIG. 4. DSC thermograms for nonisothermal crystallization at various cooling rate of (a) neat PDLLA, (b) PDLLA/ 1 wt% talc, (c) PDLLA/ 1 wt% talc/ 4 wt% ATBC, (d) PDLLA/ 1 wt% talc/ 9 wt% ATBC, (e) PDLLA/ 1 wt% talc/ 13 wt% ATBC, and (f) PDLLA/ 1 wt% talc/ 17 wt% ATBC. Exotherms are up.

nonisothermal crystallization kinetics were used. Liu et al. [51, 53] developed a model which combines the Avrami and Ozawa model, which was developed by Ozawa [54] from the Avrami equation. Ozawa [54] considered that the nonisothermal crystallization at constant cooling rate is the combination of many infinitesimal isothermal crystallizations:

$$\chi(T) = 1 - \exp\left[-\frac{k_O}{\alpha^{n_O}}\right], \quad (7)$$

where k_O and n_O are the Ozawa crystallization rate constant and exponent, respectively, and α the constant cooling rate. As for Avrami, the Ozawa exponent is dependent

on the crystal growth and nucleation mechanism. In its double logarithmic form, Eq. 7 reads:

$$\log(-\ln(1 - \chi(T))) = \log k_O - m_O \log \alpha. \quad (8)$$

As explained by Long et al. [55], the Ozawa approach predicts satisfactorily the crystallization for few polymers, such as poly(ethylene terephthalate), polypropylene, or high-density polyethylene, but it is not fully adapted to PDLLA [17]. In the present case poor linearity was obtained. The deviation from linear Ozawa model, obtained for neat and formulated PDLLA [43, 44], may be explained by the secondary crystallization which is neglected by Ozawa model, but important in our case.

TABLE 4. Avrami–Jeziorny parameters during nonisothermal crystallization of neat and formulated PDLLA.

Samples	Cooling rate (°C.min ⁻¹)	ΔH_c (J.g ⁻¹)	Primary crystallization ($5 < X(t) < 97\%$)			Secondary crystallization ($97 < X(t) < 99.9\%$)				
			n_{a1}	$k_{a1} \times 10^3$ (min ⁻ⁿ)	$k_{c1} \times 10^3$ (min ⁻ⁿ)	$t_{1/2,c1}$ (min)	n_{a2}	$k_{a2} \times 10^3$ (min ⁻ⁿ)	$k_{c2} \times 10^3$ (min ⁻ⁿ)	$t_{1/2,c2}$ (min)
Neat PDLLA	2	33 ± 3	2.9 ± 0.2	0.4 ± 0.3	20 ± 7	3.44 ± 0.13	3.0 ± 1.0	(4.8 ± 3.1) × 10 ⁻²	6.7 ± 2.3	3.66 ± 0.11
	5	3.3 ± 2.7	—	—	—	—	—	—	—	—
	10	0.4 ± 0.3	—	—	—	—	—	—	—	—
PDLLA/1 wt% talc	2	42 ± 1	9.2 ± 1.6	(3.4 ± 2.7) × 10 ⁻⁷	(1.8 ± 0.7) × 10 ⁻²	2.84 ± 0.01	2.0 ± 0.5	46 ± 35	240 ± 70	1.83 ± 0.13
	5	36 ± 3	5.8 ± 1.3	2.3 ± 2.6	270 ± 80	1.18 ± 0.03	2.0 ± 0.3	200 ± 170	700 ± 110	0.99 ± 0.08
	10	5 ± 3	—	—	—	—	—	—	—	—
PDLLA/1 wt% talc / 4 wt% ATBC	15	3 ± 2	—	—	—	—	—	—	—	—
	2	38 ± 2	12 ± 0.2	(2.1 ± 1.6) × 10 ⁻⁸	(4.3 ± 2.0) × 10 ⁻³	2.83 ± 0.10	2.1 ± 0.2	32 ± 15	180 ± 50	1.96 ± 0.15
	5	36 ± 1	8.6 ± 0.9	0.2 ± 0.1	180 ± 20	1.18 ± 0.01	1.7 ± 0.2	370 ± 140	840 ± 60	0.89 ± 0.06
PDLLA/1 wt% talc / 9 wt% ATBC	10	12 ± 4	3.6 ± 0.2	35 ± 12	710 ± 20	0.99 ± 0.01	2.4 ± 0.1	120 ± 10	810 ± 10	0.94 ± 0.01
	15	7.4 ± 4.4	3.1 ± 0.3	260 ± 80	910 ± 20	0.91 ± 0.01	2.8 ± 0.2	290 ± 70	920 ± 20	0.90 ± 0.01
	20	4.4 ± 2.9	—	—	—	—	—	—	—	—
PDLLA/1 wt% talc / 13 wt% ATBC	25	3.1 ± 1.5	—	—	—	—	—	—	—	—
	2	37 ± 1	10 ± 0.4	(1.9 ± 2.5) × 10 ⁻⁷	(1.2 ± 0.9) × 10 ⁻²	3.05 ± 0.12	2.1 ± 0.3	26 ± 16	150 ± 50	2.10 ± 0.12
	5	35 ± 1	9.2 ± 1.6	(7.2 ± 1.3) × 10 ⁻³	94 ± 4	1.22 ± 0.01	1.8 ± 0.2	310 ± 20	790 ± 10	0.93 ± 0.01
PDLLA/1 wt% talc / 17 wt% ATBC	10	29 ± 1	7.7 ± 0.8	14 ± 7	650 ± 40	1.01 ± 0.01	2.1 ± 0.2	840 ± 150	980 ± 20	0.84 ± 0.03
	15	29 ± 1	5.2 ± 0.5	100 ± 60	850 ± 30	0.96 ± 0.01	2.0 ± 0.4	1100 ± 630	1000 ± 30	0.83 ± 0.05
	20	31 ± 1	5.5 ± 0.5	150 ± 120	900 ± 40	0.95 ± 0.01	3.0 ± 2.2	850 ± 700	980 ± 40	0.84 ± 0.13
PDLLA/1 wt% talc / 17 wt% ATBC	25	26 ± 2	3.6 ± 0.6	450 ± 320	960 ± 26	0.91 ± 0.02	2.7 ± 0.1	560 ± 170	980 ± 10	0.88 ± 0.01
	2	34 ± 1	9.6 ± 0.7	(4.3 ± 4.3) × 10 ⁻⁷	(1.9 ± 1.0) × 10 ⁻²	3.00 ± 0.12	1.8 ± 0.1	44 ± 1	210 ± 2	1.93 ± 0.04
	5	32 ± 1	11 ± 0.8	(1.9 ± 2.6) × 10 ⁻³	64 ± 20	1.25 ± 0.01	1.9 ± 0.3	220 ± 80	740 ± 50	0.97 ± 0.04
PDLLA/1 wt% talc / 17 wt% ATBC	10	28 ± 2	6.9 ± 0.9	47 ± 10	740 ± 120	0.99 ± 0.01	2.3 ± 0.3	570 ± 260	970 ± 20	0.86 ± 0.03
	15	28 ± 2	6.3 ± 1.1	66 ± 31	830 ± 30	0.97 ± 0.01	2.7 ± 0.4	820 ± 180	980 ± 14	0.87 ± 0.01
	20	29 ± 2	6.3 ± 1.4	150 ± 4	910 ± 1	0.96 ± 0.01	2.2 ± 0.6	1500 ± 640	1000 ± 30	0.82 ± 0.06
PDLLA/1 wt% talc / 17 wt% ATBC	25	29 ± 3	5.4 ± 1.2	890 ± 650	980 ± 40	0.94 ± 0.01	2.0 ± 0.5	2000 ± 1400	1000 ± 40	0.81 ± 0.06
	2	35 ± 1	11 ± 1.6	(4.7 ± 6.6) × 10 ⁻⁶	(4.9 ± 7.0) × 10 ⁻²	2.84 ± 0.37	1.8 ± 0.1	47 ± 13	230 ± 20	1.83 ± 0.13
	5	33 ± 2	10 ± 1.1	(4.1 ± 1.5) × 10 ⁻²	130 ± 10	1.19 ± 0.02	2.0 ± 0.6	280 ± 120	760 ± 100	0.95 ± 0.07
PDLLA/1 wt% talc / 17 wt% ATBC	10	25 ± 2	8.1 ± 0.2	77 ± 13	770 ± 10	0.99 ± 0.01	1.8 ± 0.4	1500 ± 320	1000 ± 20	0.79 ± 0.05
	15	25 ± 4	6.3 ± 0.3	210 ± 120	900 ± 30	0.96 ± 0.01	3.2 ± 0.9	870 ± 420	980 ± 40	0.89 ± 0.04
	20	28 ± 1	6.9 ± 1.4	690 ± 600	970 ± 50	0.95 ± 0.01	1.8 ± 0.6	2000 ± 380	1000 ± 10	0.83 ± 0.01
25	29 ± 1	6.8 ± 0.4	620 ± 120	980 ± 10	0.95 ± 0.01	3.6 ± 2.2	1400 ± 650	1000 ± 20	0.87 ± 0.09	

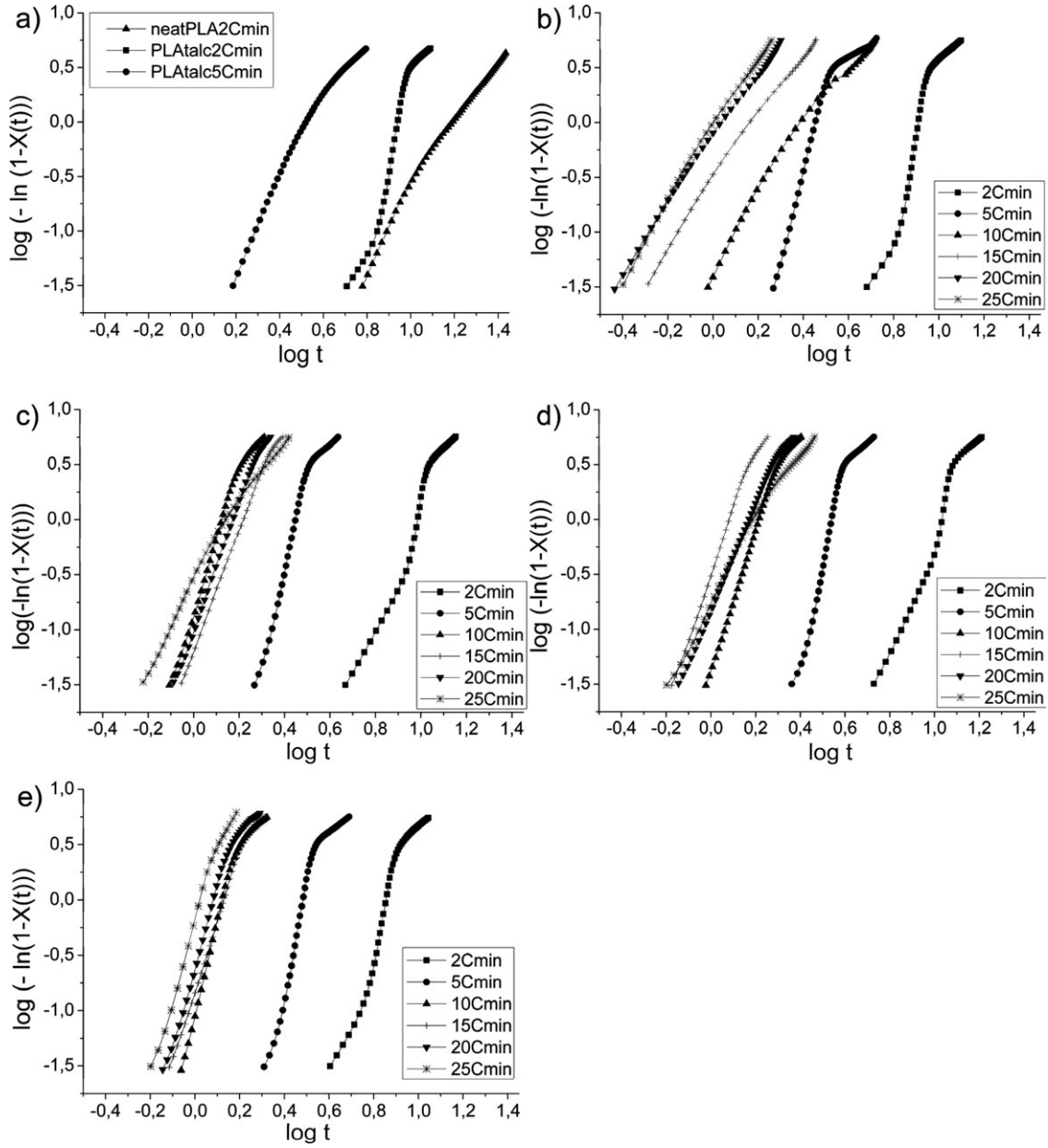


FIG. 5. Plots of $\log(-\ln(1-X(T)))$ versus $\log t$ for nonisothermal crystallization of (a) neat PDLLA and PDLLA/ 1 wt% talc, (b) PDLLA/ 1 wt% talc/ 4 wt% ATBC, (c) PDLLA/ 1 wt% talc/ 9 wt% ATBC, (d) PDLLA/ 1 wt% talc/ 13 wt% ATBC, and (e) PDLLA/ 1 wt% talc/ 17 wt% ATBC.

The Liu and Mo model [51, 53] is described by the combination of the double logarithmic form of the Avrami and Ozawa models:

$$\log k_a + n_a \log t = \log k_O - n_O \log \alpha, \quad (9)$$

From this equation, Liu et al. wrote the following equation:

$$\log \alpha = \log F(T) - m \log t, \quad (10)$$

where $F(T) = \left(\frac{k_O}{k_a}\right)^{1/n_O}$ and m is the ratio of the Ozawa exponent and the Avrami exponent ($m = \frac{n_a}{n_O}$). A value

close to one would indicate that the predictions of both models concerning nucleation and growth mechanisms are not really different. Moreover $F(T)$ is related to the value of cooling rate chosen at a unit crystallization time at which the system has reached a certain value of relative crystallinity. Therefore, a lower $F(T)$ value should reveal slower crystallization kinetics.

Figure 6 shows the plots, $\log \alpha$ versus $\log t$, for the PDLLA/talc/ATBC system at various relative crystallinity (0.2, 0.4, 0.5, 0.6, 0.8, and 0.9). The plots show poor linearization of the data points. For the composition with 17 wt% talc, the slow cooling rates 2 and $5^\circ\text{C}\cdot\text{min}^{-1}$ (0.3 and 0.7) seem to fall on another line. This follows directly

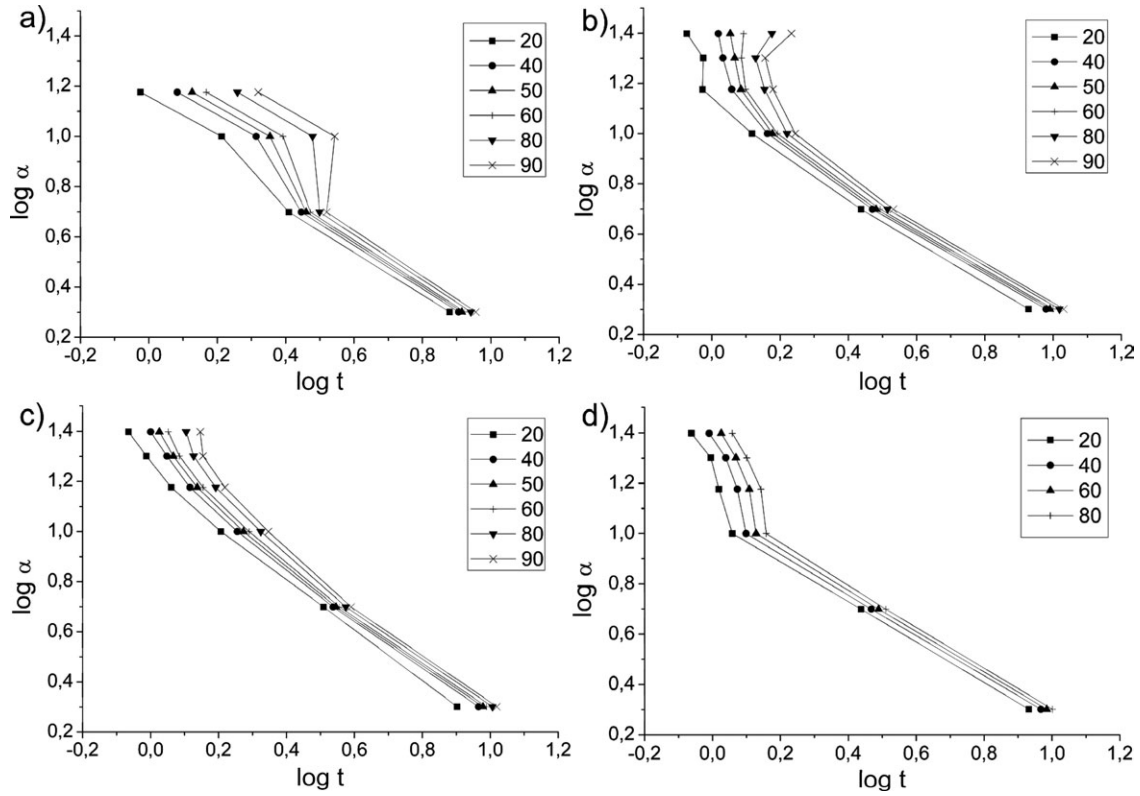


FIG. 6. Plots of $\log \alpha$ versus $\log t$ for nonisothermal crystallization of (a) PDLLA/ 1 wt% talc/ 4 wt% ATBC, (b) PDLLA/ 1 wt% talc/ 9 wt% ATBC, (c) PDLLA/ 1 wt% talc/ 13 wt% ATBC, and (d) PDLLA/ 1 wt% talc/ 17 wt% ATBC.

from the difference of the crystallization peak shapes at those cooling rates observed in Fig. 4. The Liu and Mo model parameters are given in Table 5. Moreover, the table shows that correlation coefficients (R^2) are low. The m -values are far from 1, which effectively suggest that there would be discrepancy between the predictions of the modified Avrami–Jeziorny and the Ozawa model. Furthermore, the $F(T)$ values seem to increase with increasing ATBC

TABLE 5. Liu parameters for neat PDLLA and PDLLA with 1 wt% of talc at various relative crystallinities.

Sample	$X(t)$ (%)	m	$F(T)$	R^2
PDLLA / 1 wt% talc / 4 wt% ATBC	20	0.86	14.9	0.988
	40	0.89	18.5	0.989
	60	0.90	22.0	0.992
	80	0.91	26.5	0.994
PDLLA / 1 wt% talc / 9 wt% ATBC	20	1.93	16.4	0.868
	40	2.51	24.6	0.910
	60	3.02	37.5	0.763
PDLLA / 1 wt% talc / 13 wt% ATBC	80	3.61	48.9	0.979
	20	1.45	19.4	0.989
	40	1.54	24.0	0.987
PDLLA / 1 wt% talc / 17 wt% ATBC	60	1.61	28.4	0.977
	80	1.70	34.5	0.962
	20	3.29	16.9	0.935
PDLLA / 1 wt% talc / 17 wt% ATBC	40	3.52	24.9	0.925
	60	3.63	33.1	0.920
	80	3.64	43.4	0.900

content, which would suggest a decrease in crystallization rate. This interpretation is in contradiction with the experimentally observed result of increasing crystallization enthalpy with higher plasticizer concentration. The Liu and Mo model fails apparently on the present data set, although it was applicable for example in the case of the PLA/TPP/talc system of Xiao et al. [43].

Activation Energy for Nonisothermal Crystallization

The values of the activation energy, being the energy barrier to crystallization can be calculated using Kissinger’s method [56, 57]. The Kissinger method considers the variation of the peak temperature of the crystallization exotherm and the cooling rate according the Eq. 11, where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

$$\frac{d(\ln(\alpha/T_p^2))}{d(1/T_p)} = -\frac{E_a}{R}, \quad (11)$$

The activation energy, E_a , can be estimated from the slope of the plots $\ln(\alpha/T_p^2)$ versus $1/T_p$. The E_a of the samples is negative for crystallization during cooling, which means that the reaction is deactivated by the temperature. As shown in Table 6, neat PDLLA and PDLLA with 1 wt% of talc have similar activation energy, while

TABLE 6. Activation energy values for neat and formulated PDLLA calculated with Kissinger's method.

Sample	Activation energy (kJ.mol ⁻¹)	R ²
Neat PDLLA	-101.2	0.990
PDLLA / 1 wt% talc	-101.6	0.953
PDLLA / 1 wt% talc / 4 wt% ATBC	-118.9	0.992
PDLLA / 1 wt% talc / 9 wt% ATBC	-124.2	0.992
PDLLA / 1 wt% talc / 13 wt% ATBC	-129.9	0.986
PDLLA / 1 wt% talc / 17 wt% ATBC	-146.7	0.955

E_a decreases significantly for PLA/1 wt% talc/17 wt% ATBC. This study showed that the addition of talc seems not to affect the nonisothermal crystallization of PDLLA, which is consistent with the conclusions drawn on the observation of the modified Avrami–Jeziorny constants. The addition of ATBC decreased the activation energy, which means that the process becomes more temperature deactivated. The crystallization peak would shift to lower temperatures, which is the case (Figs. 1 and 4). Indeed, the plasticizer is more efficient on the lower temperature window of the crystallization process as it furthers the mobility of polymer towards the crystallization site. Wu et al. [58] published 75.32 kJ.mol⁻¹ for PDLLA (3.3% D) and Liu et al. 126 kJ.mol⁻¹ [17]. Both authors dropped the negative sign of the cooling rate, which yields then positive activation energy. Nevertheless the dropping of the negative sign of the cooling rate is still debated [59].

Exploitation of the energy barrier, by the differential isoconversional method of Friedman [60], was carried out by Xiao et al. [43] and Li et al. [44]. Both authors reported negative activation energies. They showed that the addition of talc in PDLLA yields higher activation energies, which points to efficiency of talc in nucleating the polymer. The addition of TPP and talc brought the activation energy between the neat PLA and the PLA/talc system [43], while PEG [44] decreased E_a at contents higher than 5 wt%, which is concomitant with our results.

CONCLUSION

Nonisothermal crystallization kinetics of neat and formulated PDLLA with talc and PEG or ATBC were studied with the help of the Avrami–Jeziorny and the Liu and Mo analyses. Avrami–Jeziorny analysis revealed that the nonisothermal crystallization can be divided into two distinct stages: primary and secondary crystallization. The values of n_a suggest that the nucleation and the crystal growth of both stages are very different. The Avrami–Jeziorny analysis allowed for the investigation of the half times of the primary process on the high temperature side of the crystallization peak and the secondary process on the low temperature side. Talc showed only moderate efficiency in accelerating crystallization kinetics. Half times of the primary stage were only slightly decreased. A synergistic effect of talc with both plasticizers was observed.

PEG seemed to be the better plasticizer, but caused a large decrease in polymer molecular weight average. In the case of ATBC, the crystallization kinetics were promoted for contents higher than 9 wt%. The modified Avrami–Jeziorny half times decreased of approximately 30% compared neat PDLLA at 2°C.min⁻¹, and this decrease could be largely attributed to the drop of the half time on the low temperature side, which showed the efficiency of the plasticizer to increase chain movement. In conclusion, citrate derivatives and talc are a promising system to promote PDLLA crystallization and should be co-optimized to efficiently use their synergistic effect.

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