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Non-isothermal crystal nucleation of poly (L-lactic acid)

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ABSTRACT

The kinetics of crystal nucleation of poly(L-lactic acid) (PLLA) at non-isothermal conditions has been analyzed using fast scanning chip calorimetry, with this investigation serving as a concept study to quantitatively approach the link between the condition of cooling the melt of crystallizable polymers, the formation of crystal nuclei and the cold-crystallization behavior. The relaxed melt of PLLA has been vitrified by cooling at different rates between 1 and 1000 K s^{-1}, which suppressed melt-crystallization but led to formation of crystal nuclei depending on the cooling rate. The amount of nuclei formed during cooling was then probed by analysis of the kinetics of isothermal cold-crystallization according to Tammann's two-stage crystal nuclei development method. While crystallization of PLLA with a molar mass of about 100 kDa only occurs on cooling the melt at rates lower than 0.5 K s^{-1}, it has been found that crystal nuclei form at rates up to 50 K s^{-1}. With decreasing cooling rate between 50 and 0.5 K s^{-1} the number of crystal nuclei increases which then enhances cold-crystallization on subsequent heating, and which delays the formation and reduces the amount of additional nuclei during annealing of the glass.

1. Introduction

Poly (L-lactic acid) (PLLA) is an ecologically friendly linear aliphatic polyester which is produced from annually renewable resources and which found numerous applications for example as packaging material or in the biomedical sector; many of these applications are related to its compostability, food safety compliance, and biocompatibility/bioresorbability [1–7]. Depending on the condition of processing the melt into the solid state PLLA may partially crystallize to then yield a semicrystalline morphology which affects application-relevant properties like the stiffness, barrier properties, or the degradation/bioresorption kinetics [7–15]. For this reason, numerous investigations have been performed to characterize the crystallization behavior and to control the crystallinity, the crystallization kinetics, the spherulitic superstructure, or the crystal polymorphism [14–18].

The present work may be considered as a completion of the prior work about the crystallization behavior of PLLA, focusing here on the analysis of non-isothermal primary crystal nucleation. PLLA is a rather slowly crystallizing material with the highest crystallization rate observed at 110–120 °C. The minimum half-time of crystallization is of the order of magnitude of few minutes and increases with increasing molar mass [16–18]. Due to the low maximum melt-crystallization rate the PLLA melt can rather easily be vitrified without prior crystallization by fast cooling to temperatures lower than the glass transition temperature T_g of 60–70 °C. Systematic studies of the cooling-rate dependence of crystallization of PLLA are rare, however, were performed for PLLA with mass-average molar masses (M_w) of about 21 and 780 kDa. It was found that the low molar mass PLLA was still crystallizing on cooling at 40 K min^{-1} [19] while for the PLLA of high molar mass of M_w = 780 kDa cooling at 5 K min^{-1} was sufficiently fast to inhibit crystallization [20]. This notwithstanding, even if crystallization is suppressed, there may be formation of primary crystal nuclei during cooling and subsequent annealing in the glassy state, with the number of forming nuclei depending on the cooling rate, and the temperature and time of annealing. It has been shown for numerous polymers, including isotactic polybutene-1 (iPB-1) [21], poly (ethylene terephthalate) (PET) [22–24], poly (ε-caprolactone) (PCL) [25,26], or polyamide 6 (PA 6) [27] that these nuclei may then support cold-crystallization on subsequent heating, and contribute to the often observed difference between the kinetics of melt- and cold-crystallization. Prior studies of crystal nuclei formation of PLLA focused on the evaluation of the effects of cooling rate [20], the minimum temperature of the cooling step

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[28], and the temperature and time of a prior annealing of the PLLA glass [29–32] before subsequent heating and cold-crystallization.

In detail, for PLA with a concentration of 4.25% D-isomers and molar mass of 235 kDa it has been shown that the half-transition time of melt-crystallization at 110 °C was around 155 min while it was decreased to 105 min on cold-crystallization after prior cooling the melt at a rate of 10 K min^{-1} to 25 °C and immediate re-heating at an identical rate to 110 °C [28]. The observed result has been explained by a difference of the nucleation density, that is, by additional nuclei formed during cooling to 25 °C. Variation of the minimum temperature before cold-crystallization suggested that the nuclei density was increasing with decreasing minimum temperature with the increase, however, saturating at T_g.

The effect of the residence time below the cold-crystallization temperature onto nuclei formation has not been analyzed in the above described work, however, was studied on a PLLA homopolymer with a molar mass of 100 kDa [29,30]. In this case samples were cooled at a rate of 10^3 K s^{-1} to different target temperatures and annealed for different periods of time. Assuming that crystal nuclei only formed during isothermal annealing but not within the preceding fast cooling step, the nucleation kinetics was then probed by analysis of isothermal cold-crystallization at 120 °C. It was found that at 70 °C crystal nuclei begin to form after about 10^1 s, with the time of nuclei formation exponentially increasing with decreasing temperature; annealing at 50 °C required a minimum waiting time of 10^4 s before nuclei formation, and the extrapolated time for generation of nuclei at room temperature was estimated being about 10^8 s. The ability to form crystal nuclei in the glassy state was also shown in an independent study employing PLLA with a molar mass of 132 kDa which was cooled at a rate of 40 K min^{-1} to the annealing temperature [31].

While the temperature dependence of the nucleation rate of PLLA has been analyzed in a wide temperature range from below T_g [29,30] to 140 °C [16], based on analyses of the spherulite density or the cold-crystallization kinetics, little information is available regarding the effect of the cooling rate on nuclei formation. We are aware of a single study in which the cooling rate of a specific PLLA with a mass-average molar mass of 780 kDa was systematically varied before evaluation of the cold-crystallization kinetics as a measure of the nuclei density [20]. Samples were cooled at different rates between 5 and 300 K min^{-1} which led to complete vitrification of the melt but a systematic decrease of the enthalpy of subsequent cold-crystallization with increasing cooling rate. However, even cooling at a rate of 300 K min^{-1} did not suppress nuclei formation since a steady state/constant nuclei number, indicating its independence on the cooling rate, was not achieved. In the present work, fast scanning chip calorimetry (FSC) has been employed to further complete this initial study of the cooling-rate dependence of nuclei formation of PLLA with the aim to determine the critical cooling rate required to inhibit non-isothermal nuclei formation, and to predict the kinetics of nuclei formation in the glassy state; as such we assume and intent to prove that nuclei formation during cooling has an impact on the isothermal nucleation kinetics in the glassy state which is not only of academic but also industrial interest since it is known that the aging characteristics of the PLLA glass affects ultimate properties [10,33–35]. It is emphasized that this investigation may be considered as a concept study providing an experimental route to assess the non-isothermal nucleation kinetics of crystallizable polymers. While in this work the introduction of the concept is in foreground, a detailed analysis of the effects of molar mass and D-isomer content is in progress.

2. Experimental section

2.1. Material

The crystallization study was performed using an extrusion-grade PLLA homopolymer from Sulzer Chemtec Ltd. (Switzerland) with a melt-flow index of 6–7 g (10 $\text{min})^{-1}$ (190 °C, 2.16 kp) and residual monomer content of less than 0.3% [36]. The D-comonomer concentration of the used PLLA grade was less than 0.3%, determined by chiral gas chromatography [36], and the mass-average molar mass and polydispersity were 117 kDa and 1.8, respectively. The molar mass distribution was measured by gel permeation chromatography (GPC), using a Viscotek GPCmax VE 2002 system with a Viscotek VE 3580 RI refractive index detector. A buffer solution of dimethyl formamide (DMF) containing 10 mmol of lithium bromide was used as eluent, with a flow rate of 1 ml min^{-1}. The PLLA was dissolved in DMF at 120 °C, with the net concentration being less than 1 mg ml^{-1}. The GPC analysis was performed at 80 °C, and PMMA standards were used for calibration.

2.2. Instrumentation

Fast scanning chip calorimetry (FSC) measurements were performed using a power-compensation Mettler-Toledo Flash DSC 1 connected to a Huber intracooler TC100 for fast cooling and sub-ambient temperature operation. The calorimeters were purged with dry nitrogen gas at a flow rate of 35 ml min^{-1} to avoid icing and to protect the sample from degradation. Before placing the sample onto the sensor membrane, the FSC sensor was conditioned and temperature-corrected according to the instrument operating instructions. Furthermore, a droplet of highly viscous Wacker silicon oil AK 60,000 was equally distributed on the heatable area of the sample calorimeter, to form a thin film, for the purpose of improving the thermal contact between sensor and sample. Subsequently, the sample was placed on the sensor and heated at a rate of 10 K s^{-1} to allow slow melting and to establish a good thermal contact to the sensor. The sample mass, typically, was of the order of magnitude of 100 ng which was roughly estimated by comparison of the measured heat-capacity increment on devitrification of a fully amorphous sample in units of J K^{-1} with the mass-specific heat-capacity increment in units of J g^{-1} K^{-1}, available in the literature [37]. The PLLA was delivered in form of pellets from which specimens were prepared for the FSC analysis. We used a Slee microtome to obtain in a first preparation step thin sections with a thickness of 15 μm, which then were reduced in their lateral size to about 100 μm using a scalpel and a stereomicroscope.

Conventional differential scanning calorimetry (DSC) was applied to obtain quantitative information about enthalpies of crystallization during cooling at different rates. Note that such data are connected with an uncertainty of about 10% in FSC analyses due to the rather large error in the determination of the sample mass. We used a calibrated Mettler-Toledo heat-flux DSC 1 equipped with the FRS 5 sensor, which was connected to a Huber Intracooler TC100. The furnace of the DSC was purged with nitrogen gas at a flow rate of 50 ml min^{-1}. Samples with a mass of about 7 mg were prepared from the pellets and encapsulated into small 20 μl aluminum pans, before heating them to 225 °C for isothermal equilibration of the melt for 3 min. Samples were subjected to several cooling and heating cycles, with absence of molecule degradation ensured by analysis of multiple samples with varying cooling-rate sequence.

Polarizing optical microscopy (POM) was used to confirm the cooling-rate dependence of crystallization of the particular PLLA grade of the present work, detected by calorimetry, by analysis of the degree of completion of spherulite growth. Thin sections of