Quantification of isothermal crystallization of polyamide 12

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Quantification of isothermal crystallization of polyamide 12: Modelling of crystallization kinetics and phase composition

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HIGHLIGHTS

- Multi-phase crystallization kinetics of Polyamide 12 (PA12) has been studied by using different experimental techniques.
- Experimental results were used to parameterize and validate a new model for PA12 crystallization kinetics.
- This multi-phase model can fully describe the crystallization kinetics starting from Flash DSC experiments only.
- It is found that the bimodal dependence of the crystallization rate is due to two different nucleation processes.

ABSTRACT

The crystallization of Polyamide 12 (PA12) has been investigated using a new experimental setup which allows in-situ synchrotron Wide Angle X-ray Diffraction (WAXD) during Flash-DSC measurements. The experimental results are used to parameterize and validate a new numerical model to quantify the quiescent crystallization kinetics, under isothermal conditions, of the three important crystal structures of PA12, i.e. the, \( \gamma \), \( \alpha \) and mesomorphic phase. The experimental approach is based on nucleation and growth after quenching the material from the melt to an isothermal temperature, described by the Schneider rate equations and the Kolmogorov-Avrami expression for the space filling. The experimental overall crystallization rate, expressed in terms of the crystallization half-time, as well as the phase composition, are well captured by the model over a wide range of temperatures, i.e. between the glass transition and the melting temperature. It is shown that at temperature below and above 100°C different nucleation mechanisms are dominant causing the bimodal dependence of the crystallization rate. This work forms the basis for a full model for non-isothermal conditions for which transitions between different phase have to be taken into account.

1. Introduction

Polyamide 12 (PA12) is an engineering plastic characterized by its high strength and stiffness that make the material suitable for many different fields of applications. During the last two decades, PA12 has attracted considerable interest as material for the Selective Laser Sintering (SLS) process. Laser sintering is an Additive Manufacturing (AM) process that enables the production of three-dimensional objects, built layer by layer, starting from powdered material [1]. A layer of material is spread over a powder bed, heated up to a certain temperature, and selectively melted by a CO\textsubscript{2} laser according to the geometry of the product. As soon as the pattern is completed the powder bed moves down and a new layer of powder is spread on top of the previous one. The cooling process of the molten pattern is considered as a crucial step because semi-crystalline polymers show volume shrinkage during cooling due to the crystallization process and this effect leads to a reduction of the dimensional accuracy of the printed part. Therefore, studying the isothermal and non-isothermal crystallization kinetics of PA12 is a crucial step in order to understand and control this process. As far we are aware, not many authors have investigated crystallization kinetics of PA12 and all of them focused on the high temperature crystallization which represent the process window in SLS process [2] [3]. The goal of this work is to describe and model the crystallization kinetics of PA12 in the whole temperature range between the glass transition and the melting, to validate the model results with experimental data acquired from combining fast scanning (chip) calorimetry and wide angle X-ray diffraction (WAXD). Depending on processing conditions, PA12 shows a complex polymorphism: the \( \gamma \), \( \alpha \), \( \alpha' \) and mesomorphic phase can be formed [4] [5]. The most stable phase of PA12, obtained by slow cooling from the melt at atmospheric pressure,
is the \(\gamma\)–phase. It is characterized by a hexagonal unit cell with only one strong WAXD reflection at d-spacing of 0.42 nm. Fast quenching from the melt leads to formation of a mesomorphic structure which irreversibly transforms into \(\gamma\)–phase upon annealing. The \(\alpha\)–phase shows two strong WAXD reflections having a d-spacing of 0.37 and 0.44 nm respectively and can be obtained only under specific conditions such as high-pressure crystallization [6], casting from solution [7] and drawing just below the melting point [8]. \(\alpha\)–phase has been reported for the first time in the work of Ramesh et al. as the most stable crystalline phase at high temperatures [9]. A monoclinic structure has been assigned to both \(\alpha\)– and \(\alpha\)′–phase although the two WAXD scattering reflections of \(\alpha\)′– phase are closer compared to those of \(\alpha\)–phase. Even if the crystallization kinetics of the \(\alpha\)′– phase has been described in some papers [2] [3], there is a lack of information regarding the crystallization process at low and high undercooling and the final phase composition as a function of temperature. This can be due to the very demanding cooling rates needed to allow isothermal crystallization from the melt at very low temperatures. In the recent work of Baeten et al. a new experimental setup has been developed to acquire in-situ X-ray diffracted intensity during fast scanning (chip) calorimetry (FSC) [10]. Thanks to an “ad hoc” sample holder for the calorimetric chip and the availability of a high intensity beam and a noise-free ultrafast detector at the ESRF synchrotron center in Grenoble, it is possible to record WAXD patterns at high time-resolution. By performing simultaneously FSC and WAXD experiments, isothermal crystallization at high supercooling can be studied while being sure that the crystallization takes place under isothermal conditions. PA12, as well as many others polymers, shows a bimodal dependency in the crystallization rate when expressed in terms of peak time of crystallization and temperature. Many authors have investigated this behaviour proposing different theories, sometimes in contradiction to each other [10–12]. In the present work, we show in-situ WAXD results obtained with the new experimental setup and we describe the complex multi-phase crystallization of PA12 with a numerical model based on well defined Schneider rate equations [13] and Kolmoro-Avrami space filling expression [14] [15]. According to the experimental and numerical results, we show that the bimodal dependency of the crystallization rate is mostly due to the presence of two nucleation processes active at different degree of supercooling.

2. Theory

Crystallization of polymers is governed by nucleation and growth of ordered structures. Nuclei are formed in a polymeric melt below the thermodynamic melting point. Depending on temperature, pressure and flow conditions, they form different structures and morphologies, ranging from spherulites (in quiescent conditions) to nodules (for high supercooling) [16] or more complex structures, like shish-kebabs [17], consisting of fibrillar crystals with lamellar overgrowth (for crystallization under strong flow). For specific crystallization conditions, these structures will grow in time, with a growth rate dependent on temperature, pressure [18] and molecular orientation [19] [20] until the space is completely filled with semi-crystalline structures (impingement), if the material is given sufficient time between glass transition and melting temperature. PA12 shows a polymorphism where mesomorphic phase is formed at high undercooling and, at lower undercooling, crystalline phases are formed, i.e. the \(\gamma\)–phase and \(\alpha\)′– phase. The difference between these two crystalline structures is due to thermal expansion: the \(\gamma\)–phase shows a hexagonal unit cell in which the inter-chain and inter-sheet distance are the same. As a result of this, only one strong reflection with \(x\)-rays is visible. The \(\alpha\)′– phase has monoclinic unit cell where the inter-chain and inter-sheet distance are different resulting in two \(x\)-ray reflections. Since the hydrogen bonds push the chains away from each other, the inter-chain distance is the larger; whereas the shorter inter-sheet distance gives rise to the reflection at higher q-values (see Section 3.5) [21]. This transition is reversible, meaning that during cooling to room temperature \(\alpha\)′ always transforms into \(\gamma\). Since the transition between these two crystalline structures is governed by a thermal effect, there is a temperature region where \(\gamma\) and \(\alpha\)′ can grow at the same time inside a spherulite. To mathematically model the crystallization process, the Schneider rate equations [13] are commonly applied [18] [22]. This mathematical framework enables crystal volume fraction in time, given a certain temperature history and mathematical expressions for temperature dependent nucleation density and growth rate. Each individual crystal phase has its own thermodynamic characteristics and therefore a unique temperature dependent crystal growth rate. Therefore, limiting ourselves to quiescent crystallization at atmospheric pressure and spherulitic crystal structures for the \(\alpha\)′ and \(\gamma\)–phase, the evolution in time of the crystal volumes is given by the Schneider equations, which provide structure information in terms of number of nuclei, radius, surface and volume [13]:

\[
\phi_1 = 8\pi N_1, \quad \phi_2 = 8\pi N_2, \quad \phi_3 = 8\pi R_{\text{tot}},
\]

\[
\phi_4 = G\phi_3, \quad \phi_5 = 8\pi R_{\text{tot}},
\]

\[
\phi_6 = G\phi_5, \quad \phi_7 = S_{\text{tot}},
\]

\[
\phi_8 = G\phi_7, \quad \phi_9 = V_{\text{tot}},
\]

where \(N\) and \(G\) are (heterogeneous) nucleation and radial growth rates, respectively. The morphology of the crystalline domain is fully described by the total volume \(V_{\text{tot}}\) of the (unbounded) spherulites, their total surface \(S_{\text{tot}}\), the sum of their radii \(R_{\text{tot}}\) and the number of nuclei \(N\). In order to quantify phase composition of \(\gamma\) and \(\alpha\)′, the total volume of the crystalline domain can be divided as follow:

\[
V_{\text{tot}} = V_\gamma + V_{\alpha} = fV_{\text{tot}} + (1 - f)V_{\text{tot}},
\]

where \(f\) is a temperature dependent weighting coefficient; \(f = 1\) for relatively low temperatures (\(\gamma\) only) and \(f = 0\) for relatively high temperatures (\(\alpha\)′ only). To model the multi-phase crystallization kinetics of PA12, we follow the approach that Van Drongelen et al. developed and validated for isotactic polypropylene [18]. They proposed that every phase generates a crystal volume fraction growing with its own growth rate starting from only one available nuclei reservoir. At each timestep, the number of nuclei newly generated in the reservoir is divided over the different crystal phases according to their momentary growth rate. For example, at high temperatures where the \(\alpha\)′–phase is thermodynamically favoured (expressed by its high growth rate), the majority of available nuclei will be assigned to \(\alpha\)′–phase. Conversely, at temperatures where \(\gamma\)–phase has high growth rate, the majority of nuclei that are created will be forming \(\gamma\)–phase crystals.

\[
f = \frac{G}{\Sigma G}.
\]

Although \(\gamma\) and \(\alpha\)′ can grow together in the same spherulite, we model these two crystalline structure as two different phases with their own growth rate and we define the amount of nuclei grown in a specific phase with Equation (6), i.e. using \(N_i = f N_i\). The set of Schneider rate equation for \(\gamma\) and \(\alpha\)′ structure becomes:

\[
\phi_{1,i} = 8\pi N_i, \quad \phi_{2,i} = 8\pi R_{\text{tot},i},
\]

\[
\phi_{3,i} = G\phi_{2,i}, \quad \phi_{4,i} = \phi_{2,i} - 8\pi R_{\text{tot},i},
\]

\[
\phi_{5,i} = G\phi_{4,i}, \quad \phi_{6,i} = S_{\text{tot},i},
\]

\[
\phi_{7,i} = G\phi_{6,i}, \quad \phi_{8,i} = V_{\text{tot},i},
\]

where \(N_i\) and \(G_i\) are the nucleation density and growth rate, respectively. Subscript \(i\) denotes the different phases \(\gamma\) and \(\alpha\)′. According to the work of Androsch et al. the formation of mesomorphic phase occurs at high supercooling from the melt which leads to a nodular non-crystalline structure which extends to larger length scales than crystal
lamellae [16] [23]. Based on this observation, the morphology of PA12 mesomorphic phase is described as discs with a thickness $d_{\text{m}} = 0.5\mu \text{m}$ and the set of Schneider rate equations for the mesomorphic phase becomes:

$$\dot{\phi}_{1,\text{m}} = 2\pi d_{\text{m}} N_{\text{nm}},$$

$$\dot{\phi}_{2,\text{m}} = 2\pi d_{\text{m}} N_{\text{nm}},$$

$$\dot{\phi}_{0,\text{m}} = G_{\text{m}} \phi_{1,\text{m}},$$

$$\phi_{1,\text{m}} = S_{\text{int,\text{m}}},$$

$$\phi_{2,\text{m}} = V_{\text{int,\text{m}}}.$$  

(11) (12) (13)

2.1. Nucleation and growth rates

For quiescent crystallization from the melt, two different nucleation mechanisms are reported [12,16]: heterogeneous nucleation, which is predominant at low supercooling and is based on the interactions with surface or contaminants that reduce the free energy of the nuclei, and homogeneous nucleation which originates nuclei from the pure supercooled melt. To quantify the number of homogeneous nuclei, the classical nucleation theory [24] has been implemented as followed:

$$N_{\text{hom}} = N_0 \exp\left(-\frac{\Delta G}{k_B T}\right),$$

with the free energy of formation of a nucleus from the melt, $\Delta G$, given by:

$$\Delta G = \frac{32\sigma^2 \zeta (T_{\text{m,inf}}) h}{k_B \Delta h^2 T^3 \Delta T^2},$$

and the pre-exponential factor $N_0$ equal to:

$$N_0 = \frac{k_B T N_0}{h \left(V_m \exp\left(-\frac{U}{R(T-T_w)}\right)\right)},$$

(14) (15) (16)

In the Equations (15) and (16), $k_B$ is the Boltzmann’s constant, $T_{\text{m,inf}}$ is the equilibrium melting temperature, $\sigma^2 \zeta$ is the product of the side and interfacial energy, $\Delta h$ is the heat of fusion, $\Delta T$ is the degree of supercooling, $T_{\text{m,inf}} - T$, $N_0$ is the Avogadro number, $h$ is the Planck’s constant, $V_m$ is the molar volume, $U$ is the activation energy for a short-range diffusion across interface and $R$ is the gas constant. Between these parameters only the product between $\sigma^2$ and $\zeta$ is unknown and difficult to measure and, therefore, it was used as a fitting parameter. The total nucleation rate for each crystal phase $i$ is the sum of heterogeneous and homogeneous rate shown in the Equation (17):

$$N_i = \frac{dN_{\text{het},i}}{dt} + N_{\text{hom},i},$$

(17)

where the heterogeneous nucleation density, $N_{\text{het},i}$, is a function of temperature captured by:

$$N_{\text{het},i}(T) = N_{\text{ef}} \exp\left(-c_i (T - T_{\text{ef}})\right),$$

(18)

where $N_{\text{ef}}$ is the nucleation density evaluated at the reference temperature $T_{\text{ef}}$ and $c_i$ is a constant. During crystallization, every phase $i$ generates a crystal volume fraction $\phi_{\text{m},i}$, growing with its own growth rate $G_i$, starting from only one available nuclei reservoir, including heterogeneous and homogeneous nuclei. Therefore, the instantaneous nucleation rate for a given crystal form is defined by:

$$N_i = \int \frac{dN_{\text{het},i}}{dT} + N_{\text{hom}},$$

(19)

In the work of Hoffman et al. an equation was derived to describe growth rate as function of temperature yielding to the well known bell-shape rate curve [25] [26] [27]. In our model we use a relatively simple empirical relation, which is able to capture the growth rate for many different polymers rather well [18] [28] [29].

$$G_i(T) = G_{\text{max},i} \exp\left(-c_i (T - T_{\text{ef}})^2\right).$$

(20)

In Equation (20), $G_{\text{max},i}$ is the growth rate of the crystal phase $i$ evaluated at the reference temperature $T_{\text{ef},i}$. During multi-phase crystallization, every nucleus can grow in time, with a specific growth rate, into different crystalline structures according to temperature and pressure, until the space is completely filled and impingement occurs. To account for impingement (crystals touching each other), space filling is calculated from undisturbed volume fraction using the Kolmogoroff-Avrami theory:

$$\xi(t) = 1 - \exp(-\phi_0(t)).$$

(21)

Equation (21) does not give the space filling contributions $\xi$ of every single phase. Therefore, a rate version of Equation (21) has been implemented in the model.

$$\dot{\xi}_i = (1 - \xi) \phi_0,$$

(22)

In this expression we do not take into account the transformation of $\alpha'$-phase into $\gamma$-phase (upon cooling) or the other way around (upon heating) since we consider isothermal experiments only and, therefore these transitions are not occurring. Also the transformation of mesomorphic phase into $\alpha'$ or $\gamma$-phase upon heating and melting of different phases are not incorporated here. This would complicate things without any reason for the work presented here. Such extra terms which make Equation (22) more general, i.e. applicable for any time dependent thermal history, will be part of soon upcoming numerical approach. The set of Schneider rate equations 7–13 is numerically integrated with a built-in Matlab solver for ordinary differential equations to compute $\phi_{\text{m},i}$ and $\phi_{0,i}$ [30]. The input for the model is the thermal history and the crystallization kinetics expressed in terms of peak time of crystallization measured by Flash DSC. By manually fitting the crystallization rate, all the parameters for heterogeneous nucleation density, homogeneous nucleation rate and growth rates of every polymorph are optimized in such way that the calculated peak time of crystallization corresponds to the experimental data. With all the material functions known, the model is validated by describing the phase composition as function of crystallization temperature measured with in-situ X-ray during FSC experiments.

3. Experimental

3.1. Material

The material studied in this work is a commercial polyamide 12 (PA2200, EOS) provided as virgin powder. The specified glass transition temperature is $42^\circ\text{C}$ and the melting point $178^\circ\text{C}$.

3.2. Experimental approach

The crystallization kinetics of PA12 is studied at atmospheric pressure in a wide range of temperatures using different experimental setups. Part of the experimental data are used to determine the model parameters and part is used to validate the model in terms of crystallization rate and phase composition, the heterogeneous nucleation density and $\alpha'$-phase growth rate. The experimental approach can be summarized as follows:

- Flash DSC experiments have been performed to quantify the iso-thermal crystallization kinetics of PA12 in terms of half time of crystallization. These experimental data are then used with the multi-phase crystallization model to optimize the parameters for growth rates and nucleation rates of every crystal phase. By solving the set of Schneider rate equations, the model provides the parameters for the growth rate for every specific polymorph, the heterogeneous nucleation density and the homogeneous nucleation rate. All parameters of the material functions are evaluated and optimized in such way that the calculated crystallization kinetics capture the experimental data in the best way (in terms of least
3.3. Differential fast scanning (chip) calorimetry

Isothermal crystallization (IC) at high and low undercooling has been studied by means of differential fast scanning chip calorimeter FLASH DSC 1 from Mettler Toledo combined with a Huber intracooler TC100. More details about this technique can be found in Ref. [32] [33]. To prevent oxidation at high temperature, nitrogen is used as a purge gas at rate of 25 mL min\(^{-1}\). Samples with a mass between 100 ng and 1 µg are cut from compression moulded films and placed onto the chip. The applied thermal protocol consists of a two heating runs to 220°C for 1 s to condition the specimen, followed by fast cooling to the desired temperature \(T_{\text{iso}}\) and kept for long enough time to allow full crystallization.

To quantify the isothermal kinetics, the peak time of crystallization is determined from the exothermal crystallization peak, see Fig. 1 (a). The reciprocal peak time is proportional to the crystallization kinetics and it is considered as an appropriate and reliable measure of phase transformation rate.

3.3.1. Incomplete isothermal crystallization

Due to the very small size of the sample and to the fact that at high temperature PA12 crystallizes relatively slow, it is very difficult to determine the maximum of the heat flow during isothermal crystallization at high temperature, i.e. crystallization temperatures higher than \(\sim 140^\circ\text{C}\). Therefore, to investigate the isothermal crystallization at temperature close to the melting temperature, where PA12 fully crystallizes after relatively long times, a different thermal protocol is applied. This specific thermal protocol has been already used in the work of Androsch et al. [34] and it consists of two heating runs to 220°C for 1 s to condition the specimen, followed by quenching the material to the isothermal temperature and kept for different times. After the isothermal step, the sample is quenched below the glass transition and heated up to 220°C at 1000°C s\(^{-1}\) to quantify the melting enthalpy. We refer to these experiments as incomplete isothermal crystallization (ICC). From Fig. 1 (b) it can be seen how the enthalpy of melting increases with increasing annealing time at the isothermal temperature (peak 3). At relatively short annealing time, where PA12 does not crystallize or partially crystallizes, three distinct peaks are visible: one exothermic peak, characteristic of cold crystallization (peak 1 in Fig. 1 (b)); one endothermic melting peak at low temperature which shows always the same enthalpy as peak 1 and another endothermic peak at high temperature characteristic of the fusion of a much more stable structure created during the annealing time. The peak time of crystallization is then evaluated by plotting the normalized enthalpy of fusion as function of the annealing time [34].

3.4. Optical microscopy and standard DSC

In order to measure the growth rate of the \(\alpha'\)-phase, optical microscopy and standard DSC experiments are carried out. Because of the limited magnification of the microscope and cooling rates achievable with the hot stage, only a relatively small temperature range can be investigated. This is the temperature range where PA12 crystallizes in the \(\alpha'\)-phase. Moreover, while measuring the growth rate with optical microscopy is simple and reliable, measuring the nucleation density is more problematic. Direct observation of the morphology can be altered by many factors such as interaction with a surface and conversion between number of nuclei observed in a plane to volumetric nucleation density. Therefore, we adopted a new thermal protocol which allows to estimate growth rate and heterogeneous nucleation density from calorimetric experiments, following De Santis et al. [31]. This method is based on multiple isothermal steps where the spherulites nucleate and grow at different temperatures. By fitting the calorimetric signal with the Kolmogorov-Avrami equation they could estimate the nucleation density and growth rate of iPP. More details on this experimental protocol can be found in Ref. [31]. Therefore, in order to measure the \(\alpha'\)-phase growth rate at lower temperatures, the De Santis experimental protocol has been carried out with a Mettler Toledo DSC823e. The thermal protocol is shown in Fig. 2. It consists of isothermal crystallization steps 2°C apart in a temperature range 160-166°C. In this range PA12 fully crystallizes into \(\alpha'\)-phase in a relatively short time. After a first heating from room temperature to 220°C, to erase the previous thermal history, the material is cooled down to the desired temperature.
isothermal temperature $T_s$ kept for enough time to allow complete crystallization and successively heated up again to 220°C. The subsequent step consists of a short isothermal step at $T_s$ for 1 min followed by a fast heating at $T_f$ to allow the growth of spherulites. Heating and cooling rates are kept constant and equal to 30°C min$^{-1}$.

As already mentioned in Section 2, the three-dimensional growth of spherulites can be expressed in terms of number of nuclei with radius $R(t)$ growing in time. For the specific experimental procedure used here, Equation (21) can be rewritten in terms of volumetric nucleation density and growth rate as follows:

$$
\xi(t) = 1 - \exp(-\phi_i(t)) = 1 - \exp(\frac{4}{3}N(T_s)(G(T_s)t)^{\eta})
$$

(23)

where $N$ is the heterogeneous nucleation density, $G$ is the growth rate, $n$ is the Avrami exponent which for three-dimensional spherulites is equal to 3 and $k_i$ is the overall macroscopic crystallization rate parameter that is a function of the temperature only. To evaluate $k_i$, the heat flow rate during isothermal steps can be fitted with the first derivative of Equation (23) multiplied by the crystallization enthalpy.

$$
\frac{dQ}{dt} = \frac{d}{dt}(t - t_0) = \exp(-(k_i(t - t_0))^\eta)nk_i(k_i(t - t_0))^\eta-1.
$$

(24)

After adjusting the calorimetric signal with a baseline, Equation (24) is used to fit the isothermal calorimetric signal: the parameter $t_0$ is kept constant and equal to 1 min, the crystallization enthalpy is evaluated by normalizing the area below the crystallization peak of every experiments. In the work of De Santis, it has been shown that it is possible to estimate all the parameters for the nucleation density and growth rate (see the Equations (18) and (20)) using the overall rate constant by means of Equations (25) and (26) and only one value of growth rate measured with a different technique, e.g. optical microscopy. A Linkam TP 93 hot stage is used to melt the sample at 220°C and subsequently cool down with a cooling rate of 20°C min$^{-1}$ to a temperature of 175°C to allow isothermal crystallization. To follow the growth of the spherulites a picture was taken every 15 s with a ColorView IIIu light microscope CCD camera. To be statistically consistent, the radius of multiple spherulites was measured as a function of time.

$$
\frac{N_{i+1}}{N_i} = \left(\frac{k_{ij}}{k_i}\right)^3
$$

(25)

$$
\frac{G_{i+1}}{G_i} = \left(\frac{k_{ij}}{k_i}\right)^3
$$

(26)

This rather new experimental/numerical approach can be applied for isothermal crystallization of spherulites starting from heterogeneous nuclei of only one crystal phase. Therefore the calorimetric method proposed by De Santis et al. can describe only high temperature crystallization where PA12 fully crystallizes into $\alpha'$- phase and heterogeneous nucleation is predominant. To determine the required one value of the growth rate, optical microscopy experiments are carried out with an Olympus BX51 microscope.

3.5. In-situ X-ray during FSC

In-situ wide angle X-ray experiments during FSC were performed at the Dutch-Belgian (DUBBLE) beamline BM26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A FLASH DSC 1 is extended with an "ad hoc", X-ray accessible, sample holder for the calorimetric chip and a pulse generator which ensures synchronization between the calorimetric experiments and WAXD acquisitions. The sample holder was flushed with nitrogen as a purge gas and placed at 10 cm from a Pilatus 300 K detector. For further details about the experimental setup see Ref. [10]. The applied thermal protocol is the same described in Section 3.3. Despite the high intensity of the beam and the availability of a noise-free ultrafast detector, the acquired diffracted intensity is very low resulting in poor counting statistic due to the very small size of the sample and a short acquisition time. This problem was solved by repeating 50 times the thermal protocol and by summing the acquired WAXD patterns taken at the same temperature. Therefore, for every isothermal protocol a new sample has been used to avoid possible degradation due to long total exposure to X-rays. Moreover, the degradation has been checked comparing the calorimetric signal of every repetition. For each calorimetric chip sensor, a background pattern has been acquired and the integrated intensities are normalized to the WAXD integral to compare the results from different thermal protocols. Nevertheless, by averaging 50 times the same experiments lead to a time-shift which did not allow us to directly quantify the crystallization kinetics, i.e. phase changes as a function of time. Therefore, the in-situ measurements are used to determine the final crystal composition after isothermal crystallization. The degree of crystallinity and the crystal fractions have been calculated with a deconvolution procedure, based on the fitting of the sum of Gaussian and Lorentzian functions of the WAXD intensity. The amorphous halo is taken from the first two frames acquired at the beginning of the isothermal crystallization, where the material did not start to crystallize yet. The deconvolution procedure distinguishes every crystal phase by fitting the corresponding peaks: hexagonal for $\gamma$- and mesomorphic phase and monoclinic for $\alpha'$- phase [4,5].

We fitted the mesomorphic phase characteristic peak from the WAXD frames taken at isothermal temperature where PA12 fully transforms into mesomorphic phase, i.e. crystallization temperatures close to $T_s$. When the mesomorphic phase peak was not able to completely capture the WAXD intensity, it is assumed that crystallization into $\gamma$-phase starts taking place. In this way we could fit the characteristic $\gamma$-phase diffraction peak and quantify its crystal fraction. At high temperature, due to thermal expansion, the hexagonal unit cell of $\gamma$-phase transforms into a monoclinic unit cell characteristic of $\alpha'$- phase. The monoclinic unit cell shows two diffraction peaks relatively close to each other making the quantification of this crystal fraction more intuitive. However, the shape of two characteristic peaks of $\alpha'$- phase is fitted from WAXD frames taken at 170°C where PA12 is fully crystallized into $\alpha'$-phase. At such high temperature the distance between the two $\alpha'$ diffraction peaks is larger but the shape of the peaks remains constant. In Fig. 3 two examples of deconvolution are shown: the WAXD pattern at 90°C shows the characteristic peaks of mesomorphic and $\gamma$-phase in black and red line respectively; the WAXD frame at 170°C is used to define the width of the two diffraction peaks of $\alpha'$- phase for the decomposition procedure. As reported by Hiramatsu et al. [6], the meso and $\gamma$ diffraction peaks are very similar with the $\gamma$ peak slightly sharper than the one of mesomorphic phase. Phase composition is calculated with Equation (27) where $A_i$ is the area of the crystalline peaks of each phase and $A_{am}$ is the area of the amorphous halo.
The degree of crystallinity $\chi_i$ is plotted as a function of crystallization temperature in order to show PA12 phase transformations and validate model results.

4. Results and discussions

4.1. Differential fast scanning calorimetry results

Isothermal experiments were carried out by means of Flash DSC in the entire range of temperature between the glass transition and melting temperature. The peak time of crystallization is determined by measuring the maximum heat flow rate during isothermal analysis or, for the incomplete isothermal crystallization (IIC) by taking the annealing time corresponded to normalized melting enthalpy of 0.5 (see Fig. 4 (a)). By plotting the peak time of crystallization on a logarithmic scale as a function of the crystallization temperature, we obtain a clear representation of phase transformation rate of the material (see Fig. 4 (b)). Note that the crystallization rate is proportional to the reciprocal of the peak time of crystallization, meaning that high peak times result in slower crystallization rate.

Also, the standard DSC results were carried out in the high temperature range are shown. These sets of data (IC, IIC and standard DSC) follow the same trend and overlap at high temperature, confirming that there are no systematic experimental errors. Two regions can be distinguished marked by a transition temperatures at $\sim 100^\circ\text{C}$; a region at lower temperature where mesomorphic phase prevails, followed by a range where, depending on the temperature, PA12 can crystallize into $\gamma$-phase or $\alpha'$-phase. The bimodal dependency of the peak time is characterized by the presence of two maxima: one absolute maximum at $\sim 70^\circ\text{C}$ and one local maximum at $\sim 120^\circ\text{C}$. It can be seen that, although the temperature is approaching the glass transition temperature, at high undercooling the crystallization rate decreases but is still relatively high. It has been proposed that the bimodal shape of the crystallization rate curve is related to the presence of different nucleation mechanisms: homogeneous and heterogeneous nucleation respectively at high and low undercooling [11] [12]. In the work of Rhoades et al. the crystallization rate of two different PA11 grades is compared [11]. Both these grades show a bimodal distribution in the characteristic crystallization time. The low-temperature process was found to be grade-independent, while the high-temperature crystallization rate strongly depends on the specific PA11 grade and hence the amount of nucleating additives. This is a clear illustration that crystallization at high temperature is dominated by heterogeneous nucleation, while low-temperature processes are dominated by homogeneous nucleation and, therefore, grade-independent.

4.2. Material function optimization

Fig. 5 (a) shows the crystallization rate as function of temperature evaluated by the model described in Section 2: symbols are experimental points collected with Flash DSC and standard DSC experiments and dashed lines are model results. By solving the set of Schneider rate equations, the model gives in output information about growth rates of each polymorph, heterogeneous nucleation density and the homogeneous nucleation rate of PA12. The growth rates, $G_{m}$, $G_{\gamma}$ and $G_{\alpha'}$ are evaluated such that the calculated peak time of crystallization corresponds with the experimental values. Our optimization strategy can be summarized as follow:

- according to literature [4] [5], at high temperature PA12 fully crystallizes into $\alpha'$-phase and heterogeneous nucleation is dominant, so we determine the parameters for $G_{\alpha'}$ and $N_{het}$ by fitting the high temperature crystallization kinetics expressed in terms of peak
time of crystallization (blue line in Fig. 5);  
- by fixing the heterogeneous nucleation, i.e. $N_{\text{heter}}$ is the source for the $\alpha'$- and the $\gamma$-phase, the parameters for $G_{\alpha}$ are evaluated by fitting the crystallization kinetics in the range of temperatures where $\gamma$-phase is predominant (red line in Fig. 5);  
- mesomorphic phase can be formed only at high undercooling where homogeneous nucleation is predominant. In this way, we determine the parameters for mesomorphic phase growth rate and homogeneous nucleation rate (black line in Fig. 5).

To quantify the homogeneous nucleation rate, the $\Delta h_f$ is taken from Ref. [35] and the product $\sigma \zeta$ is used as fitting parameter. To check how sensitive the model is, multiple simulations have been run by varying this fitting parameter. The results of these simulations are shown in Section A.1. It can be seen that a slightly change in $\sigma \zeta$, results in a considerable variation on the final fitting result. By choosing $\sigma \zeta$ equal to 4.47 [J/m$^2$], the model can capture the bimodal dependency of crystallization rate in the whole range of temperatures quite well. Moreover, this value is in good agreement with the estimated value of McFerran et al. [35]. At temperatures close to the glass transition, the rate of crystallization does not slow down as we would expect, showing much faster kinetics compared to temperatures close to the melting point. This support the idea that the crystallization kinetics at temperature close to the glass transition and the melting is governed by two different processes, i.e. homogeneous and heterogeneous nucleation. It can be seen that the complete 3-phase model can describe the bimodal dependence of crystallization rate rather well: it shows two maximum points at 71$^\circ$C and 117$^\circ$C and a crossover temperature between the two bells at 95$^\circ$C in good agreement with the experimental data.

As a result of the fitting of the crystallization kinetics, the model provides the parameters for all material functions and crystal phase composition as a function of crystallization temperature (see Fig. 5(b)). The resulting values of the parameters for heterogeneous nucleation density are listed in Table 1. For the homogeneous nucleation rate, only $\sigma \zeta$ has been used as fitting parameter while the $\Delta h_f$ and $T_m$ are taken from literature [35] [3].

<table>
<thead>
<tr>
<th>$\Delta h_f$ [J/m$^2$]</th>
<th>$\sigma \zeta$ [J/m$^2$]</th>
<th>$T_m$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75 $\times$ 10$^4$</td>
<td>4.47 $\times$ 10$^{-6}$</td>
<td>$-13.2$</td>
</tr>
</tbody>
</table>

For $N_{\text{heter}}$, the corresponding parameter values are given in Table 2. The evaluated growth rates are shown in Fig. 6 (a), the heterogeneous nucleation density and the homogeneous nucleation rate in Fig. 6 (b). The corresponding parameter values are given in Table 2. At high undercooling, $G_{\alpha}$ is predominant, after a transition region where the $G_{\alpha}$ and $G_{\gamma}$ are comparable, at temperature higher then 95$^\circ$C, the $\gamma$-phase becomes faster until 130$^\circ$C where $\alpha'$- phase starts to become dominant. Because in our model the distribution of nuclei to every phase is defined by the ratio of the growth rates (see Section 2), we expect to see at the intersection temperature of the two growth rates an equal crystal phase composition. While $\gamma$- and $\alpha'$- phase have comparable $G_{\text{max}}$ (see Table 2), the mesomorphic phase growth rate is two orders of magnitude lower. This is in good agreement with the experimental results and with the hypothesis that faster crystallization rate at low temperature is not related to growth but primarily to different nucleation rate mechanisms.

It can be seen that at high undercooling the number of homogeneous nuclei formed from the super-cooled melt per unit volume and per second is very high and, although the $G_{\alpha}$ is relatively small, this leads to a faster crystallization kinetics. This clearly relates the high temperature maximum point in the crystallization rate curve to growth processes: in this temperature range, $\gamma$- and $\alpha'$- phase growth rates show the fastest rate. The homogeneous nucleation rate does not slow down at the glass transition, it can still generate a large number of nuclei even at room temperature. This behaviour has already been reported for PA6 and PLLA in the works of Androsch et al. [36] [37] [38]. The mechanism of homogeneous nucleation seems to be independent on the amorphous state but it leads to formation of nuclei both in the glassy or devitrified state.

The effect of a larger number of nuclei formed at high undercooling is shown in Fig. 5 (a), where two model simulations are compared: the black dashed line is the final fitting of the crystallization rate where the overall nucleation rate is expressed with Equation (17); while the gray dash line is the fitting result without considering the homogeneous nucleation rate ($N_{\text{heter}} = 0$). It is quite clear that forcing the homogeneous nucleation rate to zero, the model cannot capture the experimental points at low crystallization temperature because the homogeneous nucleation, although strongly increasing for lower temperatures, is not able to speed up the crystallization rate to such short half-times of crystallization. To validate the results, standard DSC
experiments according to the De Santis et al. approach are carried out which apply for the high temperature range, i.e. for heterogeneous nucleation and \(\alpha'\)-phase growth rate. The combined in-situ X-ray Flash DSC results are used to validate the model over the whole range of temperatures, but now in terms of the crystallization half-time and the phase content.

### 4.3. Model validation: standard DSC results

Heterogeneous nucleation density and \(\alpha'\)-phase growth rate are estimated by means of standard DSC according to the experimental approach proposed by De Santis et al. [31]. The calorimetric signal has been fitted by Equation (24) and the results are shown in Fig. 7.

It is evident that the Equation (24) can describe the experimental heat flow signal during isothermal crystallization quite well, allowing us to evaluate the overall macroscopic crystallization rate parameter \(k_0\). It can be seen that the resulting heat flow peaks after a step at \(T_i\) (Fig. 7b), become narrower compared to those obtained with complete isothermal crystallization at \(T_i\). This is due to the fact that extra nuclei are formed at \(T_i\) that grow at \(T_f\) after the temperature step. Once \(k_0\) for each step is known, by combining Equations (25) and (26) with only one value of growth rate measured with a different technique, e.g. optical microscopy, we can estimate experimental values for heterogeneous nucleation density and \(\alpha'\)– phase growth rate. By means of optical microscopy analysis, the \(\alpha'\)-phase growth rate at 175°C was measured.

At such high crystallization temperature the nucleation density of PA12 is low and it crystallizes into \(\alpha'\)-phase, forming relatively large spherulites. In Fig. 8 three frames acquired 5 min apart from each other during isothermal crystallization at 175°C show the growth in time and space of one spherulite. In panel (d) the last frame taken after 4 h in isothermal conditions shows a fully crystallized PA12. It is observed that spherulites grow with constant speed. To be statistically accurate, the growth of four different spherulites is measured and the isothermal experiment has been repeated twice.

The experimental results obtained for the heterogeneous nucleation density calculated with the experimental/numerical approach proposed by De Santis et al. together with the model results obtained in Section 4.2, are presented in Fig. 9 (a). As expected, in a semi-logarithmic plot, they show a linear trend and the number of heterogeneous nuclei increases with decreasing crystallization temperature. It can be seen that Equation (18), with optimized parameters obtained with multi-phase model, can describe the heterogeneous nucleation density rather well.

In Fig. 9 (b) data for the \(\alpha'\)-phase growth rate derived indirectly from calorimetric data, optical microscopy and data taken from literature [3] are shown together with growth rates estimated by the model. All the experimental data follow the same trend confirming that there are no systematic experimental errors and they overlap the \(\alpha'\)– phase growth rate evaluated with the model in Section 4.2.

### 4.4. Model validation: in-situ X-ray results

While measuring heterogeneous nucleation density and \(\alpha'\)-phase growth rate is relatively simple with optical microscopy and De Santis approach, it is experimentally difficult to quantify \(\gamma\)-phase and mesomorphic phase growth rate and homogeneous nucleation rate. Therefore, these material function obtained in Section 4.2 are validated comparing the predicted crystal compositions with those obtained from the in-situ X-ray analysis. Fig. 10 shows the last integrated WAXD intensity acquired during isothermal crystallization at different temperatures. It is evident that after the summation of 50 repetitions, the signal appears to be smooth and adequate to perform the deconvolution procedure described in Section 3.5. Nevertheless, by averaging 50 times the same measurement did not allow us to use the in-situ data to quantify the crystallization kinetics of every single polymorph. The averaging procedure, unavoidably leads to a time-shift of the crystallization rate compared to the data obtained with a standard Flash DSC described in Section 4.1.

The WAXD patterns clearly show that, depending on the crystallization temperature, PA12 crystallizes in different phases and the transition between each phase is not sharp. In a range of temperatures between 80°C and 100°C, mesomorphic phase and \(\gamma\)-phase grow simultaneously, forming a 50% composition at temperature of 90°C. Similar to the meso to \(\gamma\)-phase transition, at temperatures higher than 110°C, PA12 can crystallize into a mixture of \(\gamma\)- and \(\alpha'\)-phase. In Fig. 10 (g) a clear shoulder is visible at \(q\) values lower than the characteristic \(\gamma\)-phase diffraction peak. This indicates the presence of \(\alpha'\) crystals, and the shoulder becomes more pronounced at higher temperatures where PA12 fully crystallizes into \(\alpha'\)-phase. Crystal fractions are calculated according to Equation (27) and listed for every crystallization temperature in Table 3. It can be seen that the weight fraction of crystallinity shows a constant trend with crystallization temperature with an average value of \(\sim 31\%\).

The normalized crystal fractions will be used to validate the multi-phase crystallization model. In Fig. 11 experimental data are plotted together with the crystal phase evolution evaluated with the multi-phase crystallization model.

Although, we model \(\gamma\) and \(\alpha'\) crystals as two different phases with two different growth rates, the model can capture \(\gamma\) and \(\alpha'\) phase composition rather well. At temperatures higher than 100°C, PA12 fully crystallizes into \(\gamma\)-phase until \(\alpha'\)-phase becomes predominant. PA12 crystallizes into a 50% composition of \(\gamma\)- and \(\alpha'\)-phase at temperature \(\sim 135°C\), in perfect agreement with the model results. At temperatures lower than 80°C, PA12 fully crystallizes into mesomorphic phase. In the temperature range between 80°C and 100°C, PA12 crystallizes into a mixture of \(\gamma\)- and mesomorphic phase forming, as expected, a 50% composition at temperature of 90°C where the growth rates of these two polymorphs are equal. It can be seen that the mesomorphic phase to \(\gamma\)-phase transition prediction is less accurate than the high temperature
transition. According to the experimental data, the transition from mesomorphic to \(\gamma\) phase is less sharp than the one evaluated by the model. One possible explanation can be found in the different mesomorphic phase morphology. It has been seen that, for many different polymers, crystallization at high undercooling leads to formation of metastable nodular structures. Since it is rather complicated to quantify the growth of such complex structures, they are described in model as disks growing radially in time. Therefore, Equation (20) can describe the growth of \(\gamma\) and \(\alpha'\) spherulites rather well, but it is less accurate for the mesomorphic phase structure.

5. Conclusions

The multi-phase crystallization kinetics of PA12 has been studied by using different techniques and a new experimental setup which combines thermal and X-ray diffraction analysis. All the collected experimental data confirm that PA12 shows a complex multi-phase crystallization: depending on the crystallization temperature, PA12 can crystallize in different phases and the transition between each phase is not sharp and defined. The main conclusions can be summarized as follows:

- Although the transition \(\gamma\) to \(\alpha'\) is governed by thermal processes and they can coexist together in the same spherulites, to quantify phase composition we model these two crystal structures as two different crystal phases. By fitting with the multi-phase model the crystallization kinetics expressed in terms of half time of crystallization, we could optimize all the parameters for the material functions of every specific polymorph: heterogeneous nucleation density, homogeneous nucleation and growth rates.
- As result of the fitting, the model provides the crystal phase composition as function of temperature. It is shown that the model can accurately describe the bimodal dependence of the peak time as function of crystallization temperature. We have demonstrated that the absolute maximum of the peak time of crystallization is primarily due to the presence of two different nucleation mechanisms, homogeneous and heterogeneous nucleation respectively at high and low undercooling, while the high temperature maximum is growth related.
- It is found that the growth rate of the mesomorphic phase is two orders of magnitude lower than \(\gamma\) and \(\alpha'\) phase confirming that the formation of a larger number of homogeneously generated nuclei at high undercooling leads to a faster crystallization kinetics at low temperature.
- To validate the model results at high temperature where PA12 fully crystallizes into \(\alpha'\) phase and heterogeneous nucleation is predominant, we could measure \(G'_{\alpha'}\) and \(N_{\text{het}}\) by means of standard DSC and optical microscopy according to the numerical/experimental protocol proposed by De Santis et al.. Since it is rather complicated to experimentally quantify homogeneous nucleation and growth rates at high undercooling, the model results in this range of temperature are validated comparing the crystal phase composition with the experimental data obtained with in-situ X-ray during FSC. In both cases the model can capture the experimental results rather well.

It has been shown that with our multi-phase model we can fully describe the crystallization kinetics in terms of nucleation and growth and quantify crystal phase composition starting only from Flash DSC experiments. More work is needed on modelling the kinetics of phase transition for non isothermal histories and this is part of ongoing work.
This set of experimental data is, to our knowledge, the first in-situ study during Flash DSC measurements for PA12. It has been used to validate a multi-phase crystallization model which can be used to understand and control crystallization kinetics during every isothermal and non-isothermal process like SLS.

Acknowledgement

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Table 3
Crystal phase composition for every specific polymorph at different isothermal temperature evaluated with Equation (27).

<table>
<thead>
<tr>
<th>$T_{iso}$[$^\circ$C]</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>110</th>
<th>130</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesomorphic [%]</td>
<td>33.0</td>
<td>32.0</td>
<td>31.1</td>
<td>20.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>γ [%]</td>
<td>-</td>
<td>-</td>
<td>2.8</td>
<td>12.0</td>
<td>28.1</td>
<td>15.4</td>
<td>-</td>
</tr>
<tr>
<td>α′ [%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.2</td>
<td>28.9</td>
<td>-</td>
</tr>
<tr>
<td>total [%]</td>
<td>33.0</td>
<td>32.0</td>
<td>33.9</td>
<td>32.1</td>
<td>28.1</td>
<td>32.6</td>
<td>28.9</td>
</tr>
</tbody>
</table>

Fig. 10. Integrated WAXD intensity and relative deconvolution analysis of the last frame of isothermal crystallization.

A Appendices

A.1 Effect of fitting parameters

To check the influence of fitting parameters of the model on the final results, multiple simulations have been run by varying two parameters: the product by the side and interfacial energy $\sigma \tilde{c}_2$, in Equation (15), and thickness of mesomorphic phase discs in the Schneider rate equations, $d_m$. The results are shown in Figs. 12 and 13. It can be seen that a very small variation of $\sigma \tilde{c}_2$ determines a small variation of the homogeneous rate which results in a considerable effect on the final fitting results. Regarding the thickness of the mesomorphic discs, it seems quite apparent that $d_m$ does not play a crucial role.

Fig. 11. Crystal fractions evolution as function of crystallization temperature: all the experimental data are measured with in-situ X-ray during Flash DSC.
Fig. 12. Effect of $\sigma c$ on the homogeneous nucleation rate (a) and on the overall crystallization rate (b). Squares are experimental data and lines are model results.

Fig. 13. Effect of disc thickness ($d_{\text{meso}}$) of the mesomorphic structures: squares are experimental points; dash lines are model simulations.

B Data availability

The raw data required to reproduce these findings are available on request. The processed data required to reproduce these findings are available on request.

References

[29] T.B. Van Erp, P.C. Roozemond, G.W.M. Peters, Flow-enhanced crystallization


