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Influence of post-condensation on the crystallization kinetics of PA12: From virgin to reused powder

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HIGHLIGHTS

- The effect of prolonged storage at relatively high temperature on the crystallization kinetics of polyamide 12 (PA12) has been studied by using Flash DSC.
- The results were implemented in a multi-phase crystallization model that allows us to calculate growth and nucleation rates for different PA12 crystal phases.
- It is shown that thermal annealing results in a significant increase in molecular weight due to post condensation and this reduces the crystallization rate.
- There is no noticeable effect on the crystallization kinetics at low (below 90°C) and high (above 150°C) temperature range.
- The results can provide a better insight of the effect of reusing PA12 powder the SLS process.

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ABSTRACT

The effect of prolonged storage at elevated temperatures on the isothermal crystallization kinetics of Polyamide 12 (PA12), the most used polymer in selective laser sintering (SLS), has been studied by means of Flash DSC experiments. The experimental results are described and modelled with a full multi phase crystallization model which allowed us to estimate the growth and nucleation kinetics for every PA12 crystal phase. Virgin PA12 powder has been annealed at different temperatures for different times to quantify the molecular weight evolution due to post condensation. To check the effect of thermal treatments on the final viscosity, rheology measurements have been carried out. We show that thermal annealing results in a significant increase in molecular weight and viscosity which lead to a reduction of the crystallization rate in a limited temperature range. At very low temperature the crystallization kinetics, expressed in terms of peak-time of crystallization, appears to be independent on the annealing treatment while in the temperature range between C and 150°C a significant rate reduction is observed. We demonstrate that the crystallization kinetics in this temperature range is governed by the crystal growth process, i.e. the increase in molecular weight due to post-condensation causes a reduction of the growth rate of the main crystalline phases of PA12, namely α' and γ -phase. Similar to the low temperature crystallization, at temperature higher than 150°C the annealing does not noticeably affect the growth rates and the crystallization kinetics of virgin and annealed PA12 overlap. These results can provide a better insight of the effect of reusing PA12 powder in the SLS process.

1. Introduction

Selective laser sintering (SLS) is a rapid prototyping technique where products are made layer by layer, starting from a 3D CAD geometry file. Recently, this technology has become a manufacturing technique that enables the production of end-parts in different application fields. The SLS process consists of a built tray, normally kept in an inert atmosphere and at a temperature few degrees below the

melting temperature of the polymer, where a laser provides the extra energy to locally melt a layer of material. When the layer is completed, the bed is lowered, a new layer of powder is spread on top of the previous one and the sintering process continues until the product is completely printed [1,2]. The basic advantage of the SLS process is the ability to easily produce complex geometries and customized parts. As the powder itself acts as support to the printed product, tools, such as moulds, are not needed. This speeds up the whole production process

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and reduces production costs. Nevertheless, there are still steps that can be improved. Semi-crystalline polymers crystallize during cooling in different structures depending on the cooling rate, pressure and flow; unfortunately crystallization is associated to a volume reduction that can affect the geometrical accuracy of the printed part. It is known that the temperature range between crystallization temperature (which is a function of the cooling rate) and the melting temperature is a crucial material parameter for SLS. This temperature range has to be as large as possible to reduce the shrinking process during production and to improve product accuracy [3].

Several polymers are used as starting material for SLS, most of them are based on Polyamides, specifically Polyamide 12 and Polyamide 11 [4]. Polyamide 12 (PA12) appears to be the most suitable material thanks to high flowability during powder layer fusion and high melting enthalpy and sharp melting peak [5–7]. These features are required during laser sintering to obtain a homogeneous powder layer and to melt the powder locally with high accuracy and reproducibility [8]. To be competitive with traditional melt-processed end-parts, sintered products must have adequate mechanical and surface properties which depend on the final application field. The difference in mechanical properties between laser sintered and moulded PA12 has been already investigated in a number of publications [2,9,10]. In this work, we focus on the effect of different thermal histories on the crystallization kinetics of PA12. Powder degradation, i.e. solid state post-condensation, occurs during the printing process due to the long exposure time at high temperature in nitrogen atmosphere. Depending on product dimensions, the powder can experience severe thermal conditions up to 24 h. Moreover, the powder that is not sintered is usually reused by mixing it with fresh powder. Therefore, the level of powder aging is generally unknown, leading to reduced reproducibility and poor surface quality. This phenomenon, commonly known as orange peel effect because the final surface of the printed product reminds the skin of a peeled orange, appears to be related with changes in viscosity and molecular weight of the powder [11]. It has been shown that the molecular weight increases due to solid state post condensation [12]. Normally, chain ends of PA12 react randomly with each other producing as main by-product water. Conversely, this water molecule can react with an other polymeric chain in the same but reverse reaction keeping the average molecular weight constant. These reactions, back and forth, are in equilibrium under normal conditions and are accelerated at higher temperature. Unfortunately, the atmosphere in the printer is generally flushed with nitrogen to reduce oxidative processes which also removes the water vapor produced by post condensation, pushing the equilibrium toward the formation of longer polymeric chains [13]. In the recent work of Dadbakhsh et al. the effects of aged and mixed (mix of virgin and used powder) PA12 powder on the physical powder morphology and laser sintered parts crystallinity and morphology is studied [14]. They found that aged powder has higher initial crystallinity than virgin powder and this trend reverses after printing. Moreover, while virgin powder quickly coalesces upon heating, see top page 254, aged powder continues to coalesce at higher temperature and in a broader temperature range. All these features can play a crucial role during part sintering and consolidation. In this work, we study and quantitatively describe the effect of molecular weight increase due to thermal annealing on the crystallization kinetics of PA12 starting from fully melted material. The post-condensation kinetics is described with an empirical model, which is able to capture the time and temperature dependence, and coupled with the 3.4 power law to describe the zero-shear viscosity increase. Next, the experimental results are modelled with a multi-phase crystallization model developed in our group and applied already on virgin PA12 powder [15].

2. Theory

Crystallization of polymers can be described as a two-steps process: nucleation and growth of ordered spherulitical structures. It is known

that crystal growth is a function of temperature, pressure [16], molecular orientation [17,18] and, as we show in Section 4.3, molecular weight. Spherulites will grow until impingement occurs and the space is completely filled. PA12 shows a complex multi-phase crystallization: depending on crystallization temperature and pressure, it may crystallize into different crystal phases. Cooling from the melt at $20^{\circ}\text{C min}^{-1}$ (typical cooling rate in a standard DSC) leads to the γ -phase which is considered as the most stable structure for PA12. Quenching PA12 from the melt to a temperature close to the glass transition temperature leads to a meta-stable phase, i.e. the mesophase, reported in literature as γ' -phase [19]. For both γ and γ' a hexagonal unit cell has been assigned with only one strong x-ray diffraction peak corresponding to a d -spacing of 0.42 nm [20]. The main difference in the wide angle x-ray diffraction (WAXD) patterns of these two crystal structure is related to the fact that the γ' -phase shows a broader diffraction peak, characteristic for a less ordered structure. At high temperature, e.g. a temperature higher than 135°C , PA12 crystallizes into the α' -phase, which always transforms into γ during cooling to room temperature. By drawing [21], casting from solution [22] or under high pressure [23], PA12 crystallizes into the α -phase. Both α and α' have a monoclinic unit cell with two characteristic x-ray diffraction peaks at 0.37 and 0.44 nm for the α -phase [19], and 0.436 and 0.423 nm for the α' -phase [24]. Since SLS processes are normally carried out at atmospheric pressure, the pressure dependence is neglected here. The quiescent crystallization is fully described with a set of Schneider rate equations [25] derived for each polymorph. This mathematical framework has been proved to be able to describe the crystallization kinetics in terms of nucleation and growth rates for different polymer such as iPP [16], LLDPE [26], P1B [27] and virgin, i.e. as received, PA12 powder [15]:

$$\dot{\phi}_{3,i} = 8\pi\dot{N}_i \quad \phi_{3,i} = 8\pi N_i, \quad (1)$$

$$\dot{\phi}_{2,i} = G_i\phi_{3,i} \quad \phi_{2,i} = 8\pi R_{tot,i}, \quad (2)$$

$$\dot{\phi}_{1,i} = G_i\phi_{2,i} \quad \phi_{1,i} = S_{tot,i}, \quad (3)$$

$$\dot{\phi}_{0,i} = G_i\phi_{1,i} \quad \phi_{0,i} = V_{tot,i}, \quad (4)$$

where G_i and $\dot{N}_i$ are growth and nucleation rate respectively for the i^{th} phase: γ and α' . Eqs. (1)–(4) describe the crystallization process starting from a number of nuclei, N_i , that can grow in time with a specific radius, Eq. (2), surface, Eq. (3) and final undisturbed volume of the spherulite, Eq. (4). It is worth to mention that at this stage the spherulite can grow indefinitely within an unlimited space. Later in this Section, we account for the space filling (impingement) by defining a rate-version of the Kolmogoroff-Avrami space filling equation.

Many authors have proposed a different morphology when semi-crystalline polymers crystallize at high degree of undercooling. As reported by Androsch et al. and Mileva et al., crystallization at high undercooling leads to meta-stable nodular structures [28,29]. In order to take into account the different mesophase morphologies, the Schneider rate equation are modified assuming a disk geometry with constant thickness [15]:

$$\dot{\phi}_{2,m} = 2\pi d_m\dot{N}_m \quad \phi_{2,m} = 2\pi d_m N_m, \quad (5)$$

$$\dot{\phi}_{1,m} = G_m\phi_{2,m} \quad \phi_{1,m} = S_{tot,m}, \quad (6)$$

$$\dot{\phi}_{0,m} = G_m\phi_{1,m} \quad \phi_{0,m} = V_{tot,m}. \quad (7)$$

As already proposed in our previous work [15], to model the multi-phase crystallization kinetics of PA12 it is assumed that every phase generates a crystal volume fraction starting from only one available nuclei reservoir. The number of nuclei that grow into a specific crystal phase is determined by the actual growth rate (see Eq. (8)).

$$f_i = \frac{G_i}{\sum G_i}. \quad (8)$$

Therefore, the number of nuclei allocated to a specific crystal phase becomes $N_i = f_i N$. Two different nucleation mechanisms are reported: heterogeneous nucleation, predominant at high temperature, which leads to formation of nuclei starting from heterogeneities such as impurities or catalyst leftovers; homogeneous nucleation, predominant at high undercooling, which leads to formation of nuclei directly from the supercooled melt [28,30]. To take into account both processes, Eq. (9) is implement in the model:

$$\dot{N}_i = f_i \left(\frac{dN_{het}}{dT} \dot{T} + \dot{N}_{hom} \right), \quad (9)$$

where $\dot{N}_i$ is the overall nucleation rate for the specific phase i , $N_{het,i}$ and $N_{hom,i}$ are the heterogeneous and homogeneous nucleation respectively. The homogeneous nucleation rate has been implemented in our model according to the classical nucleation theory proposed by Koutsky et al. [31]:

$$\dot{N}_{hom} = \dot{N}_0 \exp\left(-\frac{\Delta G}{k_B T}\right), \quad (10)$$

with the free energy of formation of a nucleus from the melt, ΔG , given by:

$$\Delta G = \frac{32\sigma^2\sigma_e(T_m)^4}{k_B\Delta h_f^2 T^3\Delta T^2}, \quad (11)$$

and the pre-exponential factor $\dot{N}_0$ equal to:

$$\dot{N}_0 = \frac{k_B T}{h} \frac{N_a}{V_m} \exp\left(-\frac{U}{R(T - T_\infty)}\right). \quad (12)$$

in Eqs. (11) and (12), k_B is the Boltzmann's constant, T_m is the equilibrium melting temperature, σ^2 is the side energy, σ_e is the interfacial energy, Δh_f is the heat of fusion, ΔT is the degree of supercooling, $T_m - T$, N_a is the Avogadro number, h is 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. As already mentioned earlier in this Section, we focus on the quiescent crystallization at atmospheric pressure, hence the heterogeneous nucleation density, $N_{het,i}$, is only a function of temperature defined as:

$$N_{het}(T) = N_{ref} \exp(-c_n(T - T_{Nref})), \quad (13)$$

where N_{ref} is the nucleation density evaluated at the reference temperature T_{Nref} and c_n is a constant. The temperature dependence of the growth rate is captured with Eq. (14). In literature different mathematical descriptions have been proposed such as the well known Hoffman-Lauritzen equation [32–34]. We make use of an empirical relation, easier to handle for the model, that has been proved to capture the growth in time and space of many polymers rather well [16,35,36].

$$G_i(T) = G_{max,i} \exp(-c_{g,i}(T - T_{Gref,i})^2) \quad (14)$$

$G_{max,i}$ is the growth rate of the crystal phase i evaluated at the reference temperature $T_{Gref,i}$. To finally calculate the volumetric crystal fraction, we make use of the Kolmogoroff-Avrami theory [37,38]. The space filling ξ_i of the crystal phase “ i ” is evaluated from the undisturbed volume by means of Eq. (15):

$$\xi_i = (1 - \xi) \dot{\phi}_{0,i}. \quad (15)$$

where ξ is the total space filling described as follows:

$$\xi = 1 - \exp(-\sum (\phi_{0,i})). \quad (16)$$

With all the material functions, i.e. $\dot{N}_i$ and G_i optimized according to the crystallization kinetics of fresh virgin PA12 powder [15], the model is employed to describe the crystallization rate in terms of peak time of crystallization (see Section 3.5) of thermally conditioned powder.

3. Experimental

3.1. Experimental approach

The effects of different thermal histories on the molecular weight, viscosity and, finally on the crystallization kinetics of PA12 are studied using different experimental techniques such as thermal analysis, size exclusion chromatography (SEC) and rotational rheometry. Combining the results obtained from these experimental techniques allowed us to quantify the effect of thermal treatments on the final molecular weight, viscosity and on the overall crystallization kinetics of PA12. To guide the reader toward our experimental approach, the main steps of our work are summarized below:

- virgin PA12 powder is annealed in an oven for different temperatures and times. To avoid oxidative processes, the oven is flushed with dry Nitrogen
- to determine the evolution of the molecular weight as function of temperature and time, the molecular weight of annealed powder is measured by means of SEC (size exclusion chromatography) experiments performed at selected time intervals
- the effect of the molecular weight on the final viscosity of annealed powder is studied with a rotational rheometer. The viscosity of annealed samples is measured as function of shear rate and frequency
- To quantify the isothermal crystallization of thermally treated PA12 powder, the peak time of crystallization is measured by means of Flash-DSC experiments. To solve the set of Schneider rate equations, the model receives as input the measured crystallization rate curve. As a result, all the material functions are evaluated by minimizing the difference between the calculated peak-time and the measured one.

3.2. Material

The material studied in this work is a commercial grade of polyamide 12 (PA2200, EOS) provided in powder form. To study the effect of thermal annealing on the crystallization kinetics of PA12, the as-received powder, further referred to as “virgin” powder, is annealed at different temperatures and for different times. To reproduce the real process conditions during SLS, the annealing process is carried out in a nitrogen flushed oven. Virgin powder is annealed at four different temperatures, 120°C, 150°C and 170°C, and the molecular weight is measured at selected time intervals.

3.3. Size exclusion chromatography

In order to study the temperature and time dependence of molecular weight, size exclusion chromatography (SEC) measurements are carried out with a Water 2996 column equipped with a photo-diode detector and a refractive index detector. A PMMA calibration curve is used to convert elution time to average molecular weight. About 1.5 mg of material is dissolved in 3 ml of HFIP and filtered with a 20 μ m filter. To quantify the molecular weight build-up due to post condensation during annealing the weight average molecular weight, M_w , the number average molecular weight M_n as well as M_z and M_{z+1} are measured. To check for reproducibility, every measurement is performed twice. To capture the temperature dependence of the post condensation kinetics, 120°C is chosen as reference temperature. The molecular weight measured at different temperature is then factorized by using Eq. (17) to shift and superimpose the experimental data in order to obtain a single master curve.

$$a_T = \exp\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (17)$$

Fig. 1. Viscosity (circles) and torque (squares) as function of strain.

where a_T is the shift factor, E_a is an activation energy, T is the actual temperature and T_{ref} is the reference temperature. The time dependence of the molecular weight is captured by means of an empirical equation:

$$M(t) = K_I \exp\left(\frac{t_{eff}}{\tau_I}\right) + K_{II} \exp\left(\frac{t_{eff}}{\tau_{II}}\right) \quad (18)$$

where K_I and K_{II} are kinetics constants and τ_I , τ_{II} are time-constants all fitted according to the master curves obtained with Eq. (17) and the effective time, t_{eff} , is defined by:

$$t_{eff} = \int_0^t \frac{dt'}{a_T(T)} \quad (19)$$

By multiplying Eq. (18) by the shift factors at different temperatures, the increase of molecular weight as function of temperature and time is fully described.

3.4. Rheology

A RDA III rotational rheometer with a parallel plate geometry has been used to measure the viscosity as function of shear rate and frequency. The rheometer is equipped with a temperature controlled chamber that allows us to heat up the sample to the testing temperature of 210°C. The oven is flushed with nitrogen to avoid oxidative processes. Rather than perform the measurements on powder samples, disc shaped specimens, with a 25 mm diameter and 1 mm thickness, have been prepared by means of compression moulding. About 20 g of annealed PA12 powder is placed in a square shaped mould and moulded at 220°C for 3 min and subsequently cooled down to room temperature. The viscosity, η , is measured as a function of the shear rate starting from low strain rates after waiting ~ 5 seconds to reach the equilibrium state. Similarly, the complex viscosity, η^* , is measured starting from low frequency. In order to be sure that at the applied maximum strain the viscosity shows a linear behaviour and the measured torque is high

enough to ensure accurate and reproducible results, a strain sweep is performed.

The strain sweep results are shown in Fig. 1: circles are the viscosity values and squares are the torque values as function of strain. It appears evident that a strain of 10% results in high enough torque value and the viscosity is measured in the linear regime. To quantify the zero-shear viscosity, η_0 , the experimental data are described with the Cross model [39]:

$$\eta = \frac{\eta_0}{1 + (C\dot{\gamma})^m} \quad (20)$$

where η_0 is the asymptotic value at very low shear rates and C is a constant parameter with dimension of time and m is a dimensionless constant.

3.5. Flash DSC

The isothermal crystallization of annealed PA12 at high and low undercooling has been investigated by means of differential fast scan chip calorimetry FLASH DSC 1 from Mettler Toledo combined with an Huber intracooler TC100. To investigate the effect of annealing time and temperature on the crystallization kinetics, Flash DSC experiments are carried out on PA12 samples annealed at 120°C, 150°C and 170°C for 4 and 20 h. Samples with a mass of about 500 ng of conditioned PA12 powder are prepared and placed onto the calorimetric chip sensor. To prevent oxidation at high temperature, nitrogen is used as a purge gas at rate of 25 mL min⁻¹. The sample is heated to 40°C above the melting temperature, allowed to equilibrate for 2 s, and subsequently quenched at a cooling rate of 1000°C s⁻¹, to the desired temperature. The fast cooling rate is required to prevent crystallization during cooling and ensure that the crystallization proceeds in isothermal conditions. To quantify the crystallization rate of PA12 annealed at different temperatures, the peak time of crystallization is determined from the exothermal crystallization peak (see Fig. 2 (a)) and plotted as function of temperature. The reciprocal peak time is proportional to the overall crystallization rate and it has been widely used in literature to describe the phase transformation rate of many different polymer [30,40].

To study the isothermal crystallization at high temperature, i.e. temperatures higher than 140°C, where PA12 crystallizes relatively slow and the heat flux is very low and too noisy to determine the peak time of crystallization, a different thermal protocol has been applied [41]. In this case, the sample is quenched from the melt state to the crystallization temperature and kept at that level for different “annealing” times. After each time step, the sample is first cooled down below the glass transition temperature and subsequently heated up to 220°C at 1000°C s⁻¹. The melting enthalpy is then measured, normalized and plotted as function of the annealing time. It is assumed that, when the normalized enthalpy is equal to 0.5, i.e. the 50% of conversion is reached, the corresponded annealing time is considered as the peak

Fig. 2. Exothermic heat flow during isothermal crystallization at different temperature (a); normalized melting enthalpy as function of annealing time at different crystallization temperature (b).

Fig. 3. Weight average molecular weight as function of annealing time and temperature (a); shifted data (markers) and mathematical description with Eq. (17) (b).

time. In Fig. 2 (b) the normalized enthalpy is plotted as function of isothermal time for PA12 powder annealed at 150°C for 20 h: markers are experimental data and dashed lines indicate the estimated peak time of crystallization.

4. Results and discussions

4.1. Size exclusion chromatography results

In order to measure the molecular weight as function of time and annealing temperature, SEC measurements are performed on annealed samples. The results for the weight average molecular weight, M_w , are shown in Fig. 3 (a). The same set of data can be found in Section A.1 for the M_n , M_z and M_{z+1} .

It can be seen that M_w (as well as the others average molecular weights) increase with increasing annealing time and the post condensation rate becomes faster at higher temperatures. At 150°C, already after ~20 h which is a typical printing time considering the sintering and cooling to room temperature process, the final molecular weight is twice the initial one and this effect becomes more dramatic at higher temperatures. From Fig. 3 (a) it appears evident that all the experimental data can be shifted to obtain a master curve. By choosing 120°C as the reference temperature, the temperature dependence is captured well by an Arrhenius equation, Eq. (17), with an activation energy, E_a , of 104 kJ mol⁻¹ (see Fig. 3 (b)).

Fig. 4 shows the master curves for M_n , M_w , M_z , M_{z+1} data as function of annealing time. The calculated shift factors are shown in Fig. 5 and they apply for all the average molecular weights.

To capture the time dependence of the post-condensation rate, Eq. (18) is employed. All the parameters are fitted according to the experimental data shown in Fig. 4 and they are listed in Table 1.

It appears evident that Eq. (18) describes the experimental data rather well. Combining Eq. (17) with Eq. (18), the temperature and time dependence of the molecular weight build up due to thermal treatment can be fully described. To capture the time dependence and to be able to predict the molecular weight evolution at any temperature, Eq. (19) can be solved.

The final results are shown in Fig. 6 where symbols are experimental data collected by means of SEC measurements on annealed PA12 and the lines are model descriptions. It can be seen that this empirical approach allows us to fully capture the increase in molecular weight as function of annealing temperature and time. The experimental data indicate that the post condensation kinetics is governed by two different processes, considered additive in our model (see Eq. (18)). More work is needed to fully model the post condensation kinetics in terms of reaction mechanisms. However, this is outside of the scope of this work which is to quantify and model the crystallization kinetics of PA12 powder subjected to different thermal treatments.

Fig. 4. Master curves for M_w , M_n , M_z and M_{z+1} obtained with Eq. (17): markers are experimental data and lines are fitting results obtained with Eq. (18).

Fig. 5. Calculated shift factors, K , with Eq. (17) as function of annealing temperature.

Table 1

Estimated material parameters for Eq. (18).

Molecular weight	$K_I \cdot 10^5$ [g mol ⁻¹]	$\tau_I \cdot 10^4$ [s]	$K_{II} \cdot 10^5$ [g mol ⁻¹]	$\tau_{II} \cdot 10^2$ [s]
M_n	0.732	3.410	-0.435	-1.962
M_w	1.637	0.824	-1.134	-3.226
M_z	3.381	0.754	-2.581	-5.364
M_{z+1}	5.949	1.113	-4.864	-6.918

4.2. Rheology results

To quantify the effect of the molecular weight increase on the rheological response of annealed PA12 powder, the steady state viscosity, η , and the complex viscosity η^* , are measured as function of shear rate and frequency, respectively. Experiments are carried out on

Fig. 6. M_w (a) and M_{z+1} (b) as function of annealing temperature and time: markers are experimental data and lines are model results.

powder annealed at different temperatures for 20 h. To check for reproducibility, every measurement has been repeated at least three times. The results are shown in Fig. 7 (a) where circles represent the viscosity as function of shear rate, asterisk markers represent the complex viscosity and lines are fitting results obtained with the Cross model.

As expected, the data collected as function of shear and those obtained as function of frequency overlap confirming that the Cox-Merz rule applies. It appears evident that the model is able to describe the experimental data rather well and it allows us to extrapolate the zero-shear viscosity, η_0 . The final model parameters are listed in Table 2.

The effect of the annealing treatment is dramatic: the zero shear viscosity increases of almost one order of magnitude from $5.20 \cdot 10^2$ [Pa s] for the virgin powder to $1.51 \cdot 10^3$ [Pa s] for powder annealed at 120°C and it goes up to $1.80 \cdot 10^5$ for powder kept at 170°C. The zero-shear viscosity is considered as one of the key parameter during laser sintering because it is related to the flowability of the molten powder and hence, the layer adhesion strength [11]. Mixing used powder, i.e. powder that underwent severe thermal treatments, with virgin PA12 will result in an increase of (the average) viscosity that can lead to poor surface properties (such as orange peel effect), poor layer adhesion (delamination effect) and ultimately, low part reproducibility. From Fig. 7 (b) it appears evident that the increase in zero-shear viscosity with the molecular weight follows a linear trend with a slope of 3.4 on a double logarithmic scale. This 3.4 power law, validated already for many polymers [42–44], seems to apply well on samples annealed at 120°C and 150°C whilst the data point for the powder annealed at 170°C deviates from the general trend. Nevertheless, this relation between molecular weight and zero shear viscosity combined with the mathematical description proposed in Section 4.1 for the post-condensation kinetics allows us to derive a solid predictive framework.

4.3. Flash DSC and model results

To study the isothermal crystallization kinetics, Flash DSC experiments have been carried out on PA12 powder annealed at 120°C, 150°C and 170°C both for 4 and 20 h. In Fig. 8 the peak-times of crystallization measured with the two thermal protocols described in Section 3.5 are shown for the virgin powder (squares), annealed powder for 4 h (circles) and for 20 h (crosses). Black markers represent PA12 powder annealed at 120°C and blue markers represent data collected with powder annealed at 150°C. For the sake of clarity, in Fig. 8 the set of experimental data measured on powder annealed at 170°C is not shown because it overlaps the data acquired at 120°C and 150°C. As will be clarified later in this Section, the main parameter influencing the crystallization kinetics is determined by annealing time rather than annealing temperature.

While it is well known that virgin PA12 shows a bimodal dependence of the peak-time of crystallization with the crystallization temperature, the same trend is found also for the annealed powder. This indicates that there are different processes active at different temperature: at low crystallization temperature, i.e. temperatures lower than $\sim 100^\circ\text{C}$, homogeneous nucleation generates a large number of nuclei and speeds up the overall kinetics determining the absolute minimum point in the crystallization rate curve. It appears evident that, depending on the crystallization temperature, the effect of annealing time and temperature on the crystallization kinetics is quite different. It can be seen that the peak-time of crystallization increases with the annealing process, i.e. the crystallization kinetics slows down in the temperature range between 100°C and 150°C. The crystallization kinetics at temperatures outside this range, both higher and lower, prove to be independent of annealing time and temperature. At crystallization temperatures below 100°C all the experimental data overlap those

Fig. 7. Viscosity as function of shear rate (circles) and frequency (sterisks) for powder annealed for 20 h at different temperatures, lines represent Cross model results (a); Zero-shear viscosity, η_0 , as function of the weight average molecular weight, M_w (b).

Table 2

Cross model rheological parameters obtained by fitting the experimental data in Fig. 7.

T_a [°C]	η_0 [Pa s]	C [s]	m [–]
virgin	$5.20 \cdot 10^2$	0.0034	0.5
120	$1.51 \cdot 10^3$	0.01	0.5
150	$7.50 \cdot 10^3$	0.25	0.55
170	$1.80 \cdot 10^5$	20	0.63

Fig. 8. Peak-time of crystallization as function of crystallization temperature for virgin PA12 (squares), annealed powder for 4 h (circles) and 20 h (crosses).

acquired for virgin PA12 indicating that the low temperature crystallization is not affected by post-condensation. It is well known that at high degree of undercooling crystallization is dominated by homogeneous nucleation which leads to the formation of a large number of nuclei. This crystallization process, homogeneous nucleation and growth, is not affected by the changes in molecular chain length. A similar consideration can be made at very high crystallization temperatures, i.e. temperatures higher than 150°C, where the peak-time of crystallization is in good agreement with that measured for virgin powder. At these high temperatures the crystallization kinetics is so slow that the influence of longer chains is negligible. While samples annealed at different temperatures show a comparable peak-time of crystallization, the effect of annealing time on the crystallization kinetics appears to be more relevant: already after annealing for 4 h the peak-time increases with respect of virgin powder and the effect is similar for both annealing temperatures. This difference becomes larger when PA12 is annealed for 20 h. With all the material functions known and validated in our previous work for the virgin PA12 [15], the model is used to describe and quantify the crystallization kinetics of annealed powder.

The model uses as input the applied thermal history and the material functions already optimized for virgin material. The crystallization kinetics is described by fitting the growth rates of every single

crystal phase by minimizing the difference between the calculated peak-times of crystallization and the experimental one. The nucleation rates, both homogeneous and heterogeneous, are kept constant. The homogeneous nucleation mechanism creates nuclei from the super-cooled melt, hence it is considered to be material dependent [40]. The heterogeneous nucleation is based on the interactions with surface and contaminants (such as impurities and residual catalyst) that reduce the free energy of nuclei formation, hence it is grade dependent. Since, in this work, we used the same PA12 grade used to characterize the isothermal crystallization of virgin powder, the homogeneous nucleation rate and the heterogeneous nucleation density are kept constant and equal to those optimized for virgin PA12. In the work of Dadbakhsh et al., it is proposed that un-melted core particles, usually seen after laser sintering, can act as nucleation sites leading to a different morphology between virgin and aged powder [14]. Nevertheless, in our work case, the crystallization kinetics is studied starting from fully melted samples quenched to the desired crystallization temperature; hence there are no un-melted cores that can alter the overall nucleation density.

In Fig. 9 the final fitting of the crystallization rate curves are shown: in Fig. 9 (a) the half time of crystallization of PA12 annealed at 120°C and 150°C for 4 h (black circles) is plotted together with the model results (black dashed line) in comparison with the results of virgin PA12 (green squares are experimental data and dashed line model results). The same set of data and model results can be found in Fig. 9 (b) for powder annealed for 20 h. It can be seen that the model can capture the bimodal dependence of the peak-time of crystallization rather well and shows a good agreement with all the experimental data. As expected the model results for annealed powder overlap the results obtained for virgin PA12 at crystallization temperatures close to the glass transition temperature and higher than 150°C. The dependency of the crystallization rate with the annealing time in the temperature range between 100°C and 150°C is described by the model as a reduction of the growth rates of α' -phase and γ -phase.

This is shown in Fig. 10 (a) where the growth rate of each polymorph are plotted as function of temperature, and in Fig. 10 (b) where the $G_{max,i}$ is plotted as function of the molecular weight M_w . Table 3 gives the parameters of Eq. (14) for α' -, γ - and the mesomorphic phase. After an annealing treatment of 20 h, the maximum of the $G_{\alpha'}$ and G_γ is one order of magnitude lower than in the case of the virgin PA12 powder. As expected, the mesomorphic growth rate, G_m , does not change with the annealing time and it appears to be independent of the molecular chains length. This is in good agreement with the hypothesis that crystallization at high undercooling is primarily governed by homogeneous nucleation and not by growth processes, hence the crystallization rate is not affected by the molecular weight. At high temperature, i.e. temperature higher than 150°C, where the crystallization rates of annealed powder overlap that of virgin PA12, the

Fig. 9. Peak-time of crystallization as function of crystallization temperature for virgin PA12 (squares), annealed powder for 4 h (circles) (a) and annealed powder for 20 h (circles) (b); lines are model results.

Fig. 10. Growth rates of the different crystal phases evaluated with the model (a); $G_{max,\alpha'}$ and $G_{max,\gamma}$ as function of M_w (markers) with a linear regression (dashed line) (b).

Table 3

Growth rate parameters: data for virgin PA12 are taken from Ref. [15], annealed for 4 and 20 h are calculated with the model.

parameter	virgin	annealed 4 h	annealed 20 h	units
$G_{max,\alpha'}$	$1.4 \cdot 10^{-4}$	$6.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	$[ms^{-1}]$
$c_{g,\alpha'}$	$6.7 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$	$[^{\circ}C^2]$
$T_{Gref,\alpha'}$	136	136	136	$[^{\circ}C]$
$G_{max,\gamma}$	$1.3 \cdot 10^{-4}$	$4.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$[ms^{-1}]$
$c_{g,\gamma}$	$4.9 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$[^{\circ}C^2]$
$T_{Gref,\gamma}$	123	123	123	$[^{\circ}C]$
$G_{max,m}$	$2.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$[ms^{-1}]$
$c_{g,m}$	$4.1 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	$[^{\circ}C^2]$
$T_{Gref,m}$	81	81	81	$[^{\circ}C]$

difference in growth rate of α' and γ -phase between virgin and annealed PA12 becomes negligible and both samples show the same peak-time of crystallization. During laser sintering process the powder is kept at a temperature few degree lower than the melting temperature and the laser provides the extra heat needed to melt locally the powder. When one layer is completed, the powder bed moves down and the cooling process begins. Normally, because the powder tank, i.e. the tank that contains the sintered parts, is kept at temperature of $\sim 120^{\circ}C$, crystallization occurs in the temperature range which appears to be the most affected by the increase of molecular weight and viscosity. This leads to a less homogeneous crystallization process where, depending on the aging status of the powder, the crystallization kinetics and, hence, the final properties of the products can change.

5. Conclusion

In this work the effect of post-condensation of PA12 powder on the crystallization kinetics has been investigated. To quantify the influence of thermal treatment on the molecular weight and viscosity, virgin powder of PA12 has been annealed at different temperature and for different time in a Nitrogen environment. It is shown that the molecular weight increases with annealing time and temperature. Already at $150^{\circ}C$, which is a typical process condition during sintering, after ~ 20 hours the molecular weight is twice the initial one and the increase becomes more remarkable at higher temperature and for longer annealing time. The molecular weight evolution, measured by means of SEC, is described by means of an empirical equation which allowed us to capture the temperature and time dependence. The viscosity, as well as the complex viscosity has been measured for samples annealed at different temperature. As expected, due to the increase in molecular weight, the zero-shear viscosity of annealed powder is much higher than virgin PA12 powder. The increase of the zero-shear

viscosity as function of molecular weight can be described with the 3.4 power dependence rather well. Samples annealed at $120^{\circ}C$ have a zero-shear viscosity one order of magnitude higher than virgin material and the difference becomes larger at higher temperature. It is concluded that by mixing annealed powder, i.e. recycled powder, with virgin PA12 can lead to a significant increase in the average viscosity which can result in reduced surface quality, poor layer-to-layer adhesion and, ultimately, to low reproducibility. To study the effect of thermal treatment on the crystallization kinetics, Flash DSC experiments are performed on powder annealed at $120^{\circ}C$ and $150^{\circ}C$ for 4 and 20 h. The experimental results are modelled with a full multi-phase crystallization model already validated on virgin PA12 in our previous work. This study reveals several features that can be summarized as follows:

- the model is found to be a valid and reliable framework to describe the crystallization kinetics of annealed powder. The model can capture the dependence of the peak-time of crystallization with temperature rather well and it allows us to determine the material functions for post-condensated powder, i.e. growth rates of every crystal phase.
- The effect of post-condensation on the crystallization kinetics is described by the model with a reduction of the growth rates of α' and γ -phase. The overall nucleation density/rate is kept constant and equal to the one of virgin powder. The homogeneous nucleation rate generates nuclei from the supercooled melt, hence is considered material dependent; the heterogeneous nucleation is based on the interaction with heterogeneities in the material and therefore it is considered grade dependent.
- It has been shown that the crystallization rate in the low temperature region (temperatures lower than $100^{\circ}C$) where homogeneous nucleation is predominant, expressed in terms of peak-time of crystallization, is not affected by post-condensation. All the experimental data of powder annealed at different temperature and time overlap those obtained from virgin PA12 powder. This can be explained by considering the homogeneous nucleation that generates a huge number of nuclei and, therefore, the crystallization kinetics is not governed by growth but primarily by nucleation.
- A similar consideration can be made for high crystallization temperatures (temperature higher than $150^{\circ}C$). In this temperature range both virgin and annealed powder show the same crystallization rate. This can be rationalized considering that the α' -phase growth rates of annealed powder and the one of virgin powder are comparable.
- In the temperature range between $100^{\circ}C$ and $150^{\circ}C$ the crystallization kinetics is significantly affected by the thermal treatments. Although samples annealed at different temperatures show a comparable crystallization rate, the effect of annealing time is remarkable: the crystallization kinetics significantly reduces when PA12 is annealed for 4 h and it reduces even more for powder annealed for 20 h.

This work provides basic input for a full model of the SLS process, under development in our group, see Ref. [45], that will allow for studying in detail the effect of process and material parameters and the effect of the use history of the powder.

A Appendices

A.1 SEC results

Fig. 11 shows the average molecular weight M_n , M_z and M_{z+1} as function of annealing time and temperature measured by means of size exclusion chromatography. Similarly to M_w , all the average molecular weights display an increase with time and temperature.

Fig. 11. SEC measurements results of PA12 powder annealed at different temperature and for different time.

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.

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