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Characterization of the primary and secondary crystallization kinetics of a linear low-density polyethylene in quiescent- and flow-conditions

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ABSTRACT

The primary and secondary crystallization kinetics of a homogeneous linear low-density polyethylene were characterized as function of cooling rate, pressure and flow strength. Our approach to describe primary crystallization is based on nucleation and growth of spherulites, quantified well below the melting temperature using small-angle light scattering. The description of the two-step secondary process is coupled to primary crystallization using a convolution integral, for which the parameters were determined from (fast-) differential scanning calorimetry. Extended-dilatometry was used to investigate the effect of different thermomechanical histories. Parameters were determined for an existing model that couples molecular stretch to both nucleation rate and fibrillar growth rate. Excellent agreement is shown between calculated and experimentally obtained crystallization kinetics in conditions representative for those found in real-life processing conditions. This opens the possibility to calculate in detail the evolution of and the final crystallinity structure in products such as blown film or extruded tape.

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1. Introduction

The use of ethylene and α -olefin copolymers has become widespread via the industrial implementation of metallocene type catalysts and the materials broad application in packaging industry. Also known as linear low-density polyethylene (LLDPE), the material is a substantially linear polymer with a large number of short branches, providing distinct rheological and mechanical properties, such as a relatively low shear sensitivity and a high tensile- and impact strength [1]. In order to understand the crystalline morphology of the final product as function of the shaping process, many researchers report on the crystallizability and processing-structure relation for various LLDPE resins, and focus specifically on the significant influence of the molecular branching-type, content, and distribution [2–7]. As the shaping process of polymeric products involves steep thermal gradients, high flow rates and pressure variations, studying the processing-structure relation in

industrially relevant conditions requires well defined experiments in which these variables can be controlled. As a result of the rapid crystallization process of the ethylene based polymer, the temperature window for isothermal studies is often limited to low levels of undercooling. An additional complexity with branched (semi-crystalline) polymers is found in the high levels of secondary crystallization, sometimes up to 50% of the final crystallinity, due to a continuous insertion or thickening of lamellar features inside the spherulitic geometries [8]. Many different experimental techniques were used to study crystallization from the LLDPE melt, often providing a measurement signal in which the different processes cannot be separated (easily). Therefore, most researchers prefer combined techniques of, for example, small angle light scattering (SALS), differential scanning calorimetry (DSC), and/or simultaneous small- and wide-angle X-ray scattering/diffraction (SAXS/WAXD) to obtain detailed time resolved structural information [6,9–12]. Reports on the effects of flow on crystallization of LLDPE are limited and mostly performed using shear cell devices [7,13] or uniaxial extension [14], whereas the combined effect of pressure and flow has been studied mainly to obtain melt properties using rheometry [15,16].

In some studies, the experimentally obtained non-isothermal (quiescent) crystallization kinetics are used as validation or input

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for predictive structure calculations, often using kinetic models [17–19] or physical models describing primary crystallization [20–22]. In the case of LLDPE however, the most promising approach is found in extended Avrami models to account for secondary crystallization effects [23–25]. The latter suits the implementation of nucleation and growth functions to describe primary crystallization. Hence, such a model requires accurate determination of both, the spherulitic growth rate and nucleation density in a wide range of temperatures in order to correctly describe space filling of spherulites in time. In this work, we adopted an Avrami-type model for space filling based on nucleation and growth, combined with a convolution integral to accurately describe the evolution of primary and a two step secondary crystallization during quiescent non-isothermal solidification in a large range of cooling rates. To obtain parameter values, we use a combination of SALS, DSC and fast scanning chip calorimetry (FSC) techniques. Secondly, flow induced (primary) crystallization is described for different thermomechanical histories at multiple pressures with an approach based on rheology and dilatometry, similar to earlier work performed in our group [26]. Finally, dilatometry was used to characterize the effect of flow and pressure on secondary crystallization by converting the dilation measurement in a signal similar to those measured with DSC.

2. Material and methods

2.1. Material

The material investigated is a metallocene LLDPE (ExxonMobil). It has an average butyl branch content of 1.2 mol%, a weight average molecular weight, M_w , of 94 kg/mol and a number average molecular weight, M_n , of 24 kg/mol. The interchain branching distribution is relatively narrow, as indicated by temperature rising elution fractionation (TREF) data presented in Fig. 1 and molar mass fractionation of the same material reported elsewhere [27]. Details about the TREF procedure are included in Appendix A.

2.2. Methods

2.2.1. Thermal analyses

Differential scanning calorimetry (DSC) was employed to investigate non-isothermal crystallization at relatively low cooling

Fig. 1. Normalized concentration vs. temperature during TREF of the LLDPE investigated. The elution temperature directly relates to co-monomer content.

rates. Use was made of a Mettler-Toledo 823e/700 module in combination with a Cryostat intracooler. A sample of about 5 mg was placed in a 40 μ m standard aluminum crucible. The sample was heated at 20 $^{\circ}$ C/min from 25 $^{\circ}$ C to 180 $^{\circ}$ C, held at that temperature for 5 min to erase any thermal history and subsequently cooled at rates, $\dot{T}$, of 4–20 $^{\circ}$ C/min to 0 $^{\circ}$ C. The equipment was calibrated for static temperature, thermal lag, and heat of fusion using indium and zinc. Nitrogen was used as a purging gas.

For relatively high cooling rates, non-isothermal crystallization was studied using a fast scanning chip calorimeter (FSC) Flash DSC 1 of Mettler-Toledo in combination with a Huber intracooler TC100 and UFS-1 sensors [28–30]. Samples were prepared by microtoming and microscope-aided cutting. The specimen was heated at 100 $^{\circ}$ C/s to 150 $^{\circ}$ C and kept at that temperature for 1 s, which is sufficient to remove all thermal history due to the limited sample dimensions. Subsequently, the sample was cooled to –50 $^{\circ}$ C in a range of 50–2000 $^{\circ}$ C/s. Scan rates below 50 $^{\circ}$ C/s were not investigated, the signal to noise ratio became unsatisfactory due to the low sample mass. Above 2000 $^{\circ}$ C/s, the cooling rate selected could not be maintained until the end of the crystallization process. Nitrogen was used as a purging gas, no corrections for thermal lag effects were included since the sample dimensions were considered minimal. The FSC sensor was conditioned and temperature-corrected according to the specification of the instrument provider.

2.2.2. Small angle light scattering

Small angle light scattering (SALS) combined with a temperature jump-stage experiments were performed to measure the temperature dependent spherulitic growth rate and nucleation density up to high levels of undercooling. Samples of approximately 5.5 mm in diameter, 30 μ m in thickness and a mass of 0.5 mg were prepared by melt-compression molding a small amount of granular material sandwiched between two cover glasses of 9 mm in diameter and a thickness of 150 μ m each. The specimens were placed in a custom-modified JHT-350 temperature-jump stage [31] (Linkam, Japan), which consists of two separately controlled heating stages and allows for the sample to be rapidly transferred from the hot stage, set to 150 $^{\circ}$ C, towards the cold stage, set at the desired temperature for crystallization, by means of an aluminum slide. The sample was transferred to and kept at the hot stage for 1 min to erase all structural history. Due to the large capacity of the heating stages and the small sample size, cooling rates were reported in the order of 300 $^{\circ}$ C/s [31]. Custom modifications by our group consist of a remotely controlled and air pressure driven actuator, connected to the aluminum slide, to quickly transport the sample back and forth between the stages and at reproducible speeds, see Fig. 2. Experiments were performed in duplo at each set temperature. The temperature of both stages was corrected using a calibrated K-type

Fig. 2. The custom modified JHT-350 temperature-jump stage (without top cover).

micro-thermocouple connected to a temperature readout device (USB-9162, National Instruments).

The light-source consisted of a He–Ne laser ($\lambda = 6328 \text{ \AA}$, JDS Uniphase, USA) at constant intensity which was directed perpendicularly through the sample, which itself is located in between two crossed polarizers (H_V polarization mode). The resulting pattern was projected onto a semi-transparent screen and recorded with a high-speed Orca Flash 4.0 sCMOS type camera (Hamamatsu, Japan) equipped with a 25 mm Schneider-Kreuznach Xenon lens. No corrections for transmission, refraction and reflection were made [32], since absolute intensities were not needed for our analyses. Sample to projector screen distance was 122 mm, the scattering angle was calibrated with a fine grid and pixel size was $88.75 \mu\text{m} \times 88.75 \mu\text{m}$. Images were recorded continuously in time at rates in the range of 50–200 Hz, controlled by Hokawo software (Hamamatsu, Japan) and corrected for background noise and melt contribution. Integration of the patterns was performed by using Fit2D software (ESRF, France) to obtain scattering intensity, I_q , versus the scattering angle, q . For data reduction purposes, only one lobe of the characteristic four-lobed pattern was selected for recording. A Lorentzian curve was fit to each pattern to smoothen the data and the position of the peak of this curve was determined. Experiments were performed in the set temperature range of 78–104 °C. Above 104 °C, the maximum scattering angle merges with the beamstop and the peak position could no longer be traced as function of temperature. Below 78 °C, the first scattering frames recorded already showed signs of ongoing crystallization. Here, the cooling power of the jump-stage is insufficient, and, in addition, the orientation correlation in the crystallites becomes too low to provide a clear peak.

2.2.3. Dilatometry

Dilatometry experiments were performed with the Pirouette pVTt – $\dot{\gamma}$ apparatus (IME technologies, the Netherlands) [33,34]. It allows investigation of the evolution of specific volume of polymers as a function of temperature, pressure, cooling rate and shear rate by measuring the volume change of a sample. The apparatus requires ring-shaped samples with a mass of ~75 mg, an outer diameter of 20 mm, thickness of 0.5 mm and height of approximately 2.5 mm, which were pre-produced from granular material using a Babyplast injection molding machine (Rambaldi, Italy) equipped with a custom build mold. Experiments were performed in isobaric cooling mode at pressures of 100 and 500 bar. The sample was heated to 180 °C and kept at that temperature for 5 min to erase all thermal history. Finally, the piston and die were cooled by a constant flux of air which resulted in an initial cooling rate of 1.0 °C/s (measured between 180 and 130 °C). Experiments with flow were carried out over a wide range of shear rates, $\dot{\gamma}$ (from 3 to 180 1/s) and a constant shear time of 1 s at the chosen shear temperatures.

2.2.4. X-ray diffraction

The molecular orientation of processed samples from dilatometry was investigated using 2D Wide-angle X-ray diffraction (WAXD). Measurements were performed at the Dutch-Belgian (DUBBLE) beamline BM26 of the European Synchrotron Radiation Facility in Grenoble, France [35]. The source-ray photon wavelength was set to 1.033 Å, with an X-ray beam of 300 μm in diameter. Patterns were acquired with an exposure time of 10 s. All patterns were collected by means of a Frelon CCD detector (Photonic Science, UK) with 2048×2048 pixels of $48.83 \times 48.83 \mu\text{m}$ at approximately 160 mm from the sample surface. Data was integrated, corrected for static noise, and background subtracted using the Fit2D software package (ESRF, France).

2.2.5. Rheological characterization

Small amplitude oscillatory shear (SAOS) measurements were performed with an MCR 502 Rheometer (Anton Paar, Austria), equipped with a plate–plate geometry (diameter 25 mm). The characteristic rheological properties, i.e. storage and loss moduli, G' and G'' and loss angle, δ were obtained over a wide range of temperatures (from 115 °C to 180 °C) and angular frequencies, ω (from 0.1 1/s to 300 1/s). To determine properties in the linear viscoelastic regime, the strain, γ , applied was chosen after strain sweeps and set to 5% for all measurements. Time-temperature superposition has been applied to obtain a mastercurve at a reference temperature of 160 °C.

The polymer was also characterized in simple extension using a SER2-P SER Universal Testing Platform [36] fixture hosted on the MCR 502. Uniaxial extension experiments were performed at 160 °C, using various strain rates up to the maximum achievable Hencky strain, ε_H , of four. All the experiments were performed under constant nitrogen flow to avoid sample degradation.

3. Results and discussion

First, quiescent crystallization of the m-LLDPE grade is discussed, followed by characterization of the solidification kinetics using thermal and scattering methods. Next, the crystallization model is discussed for both the primary and secondary processes. Finally, the effect of flow and pressure is characterized using rheology and dilatometry, and optimal values for scaling parameters describing flow-induced crystallization (FIC) were obtained for a model that is based on molecular stretch.

3.1. Thermal characterization

The type of polymerization process provides that m-LLDPE is a substantially linear polymer with a controllable amount of short branches. The intermolecular distribution of these side chain branches is called homogeneous when the distribution of branches between the molecules is narrow, while the sequence length distribution between branches can still be broad. The longer ethylene sequences, having a higher melting point, crystallize faster [37–39] and fold into stacked lamellae that span the spherulite from the free melt, defined as primary crystallization [8]. Quenching the melt at increasing rates smears out this process over a larger temperature range and/or postpones crystallization to lower temperatures due to insufficient time for nucleation and growth [40,41]. Crystallinity may further increase due to secondary crystallization of the shorter sequence length chain sections, even before spherulitic impingement [42]. They form lamellar stacks in the amorphous regions between the primary lamellae inside the spherulite [42,43].

The influence of comonomer content is reflected by a second peak in the crystallization process commonly observed at low temperatures in DSC [9,10]. During the lamellar folding process, the length of the side chain determines whether or not it is excluded from the crystal lattice [3,6,44]. As the already formed lamellae restrict the topological movement of the remaining sequences, these are unable to attain the chain folding process. Hence, at high levels of undercooling, a second stage of secondary crystallization yields a granular morphology consisting of small bundled structures or loosely packed ethylene sequences [6,9,10,45]. A simplified, schematic, and time discretized overview of the primary and two stage secondary process is given in Fig. 3.

For each DSC and FSC experiment, the total baseline subtracted heat capacity, or the excess heat capacity, is composed of the contributions of the crystallization processes observed, i.e. one primary and two secondary crystallization events. Peak decomposition of the signal is used to determine each process as function of

Fig. 3. Schematic time discretized overview of primary and secondary crystallization process during cooling. (1) A nucleated spherulite grows in time as function of temperature, fast growing primary lamellae are formed from the most linear molecular sequences. (2) Shorter sequence lengths induce secondary lamellar growth in the remaining amorphous regions. Lamellae gradually become thinner with undercooling according to classical theories [46]. (3) Finally, at high undercooling, free chain sections locally order into small bundled structures.

temperature, see Fig. 4. In our approach, the primary process is marked by the symmetric fraction of the sharp peak at high temperatures, and is described by a Gaussian function. During cooling, the crystallization rate increases and the remaining crystallizable material decreases, in this work we assume that this results in a symmetric release of heat as function of temperature. A pronounced exotherm with a peak at $\sim 60^\circ\text{C}$ due to bundle like features was best described using a much broader Lorentzian function. The lamellar insertion process that rapidly follows primary crystallization at slightly higher undercooling and the corresponding heat release provides the peak with high level of asymmetry. Depending on the comonomer content, a separate crystallization peak or a distinct shoulder is observable. It is assumed that the heat capacity not included in both peak functions can be fully attributed to the insertion of lamellae, see again Fig. 4, which can be described with an n -number of Gaussian functions versus temperature, representing multiple lamellar insertion processes with decreasing lamellar thickness [46]. Although it is more common to deconvolute DSC melting curves, the melting characteristics of this material consist of one clear peak only and do not allow for such a procedure. The decomposition of the DSC-signal in this wide range of cooling rates in these three contributions is, to our knowledge, not done before.

Fig. 4. Schematic of the peak decomposition process of the measured excess heat capacity.

Good fits of the peak functions to the data were always obtained, as is shown in Fig. 5, where both DSC and FSC measurements are displayed, i.e. for low and high cooling rates, including the determined peak functions.

Regarding conventional DSC experiments, crystallinity was calculated from the integrated peak, which was normalized for sample mass and cooling rate. The (linear) extrapolated heat capacity of the melt was used as a baseline [47]. The transitional enthalpy for polyethylene, $\Delta H(T)$ was taken from literature [48] and assumed to be a function of temperature only. We do not distinguish between the folding energy of lamellae and bundle-like features. For the FSC sample, the same protocol was applied, with the sample mass determined iteratively at ~ 400 ng by matching the amount of primary crystallinity calculated at the slowest cooling rate with FSC to the value obtained at the highest rate with DSC. It was assumed that in this range of cooling rates, primary crystallization was not suppressed, i.e. complete space filling is obtained.

When crystallinity is plotted versus temperature, for example for 200°C/s in Fig. 6a, it becomes clear that the primary process fully covers the first, steep increase at high temperatures. This rapid process covers a maximum of 15.2% of total crystalline volume, which corresponds to values also found by Goderis et al. [11]. At this stage, the crystallinity distribution inside the spherulites is presumed inhomogeneous (see Fig. 3). Upon further cooling, crystallinity will develop more slowly via lamellar insertion, the rather sharp transition point at approximately 50°C corresponds to bundle-like structure formation.

Both techniques used cover together a wide range of cooling rates, albeit with a large gap in between roughly 10^0 and 10^1°C/s , see Fig. 6b. At low rates a more or less constant crystallinity distribution was observed for primary- and for both stages of secondary crystallization and for all conditions. In the case of the FSC scan rates, a gradual decrease of the total crystallinity was obtained mainly caused by a reduced level of lamellar insertion, a process which is slow compared to primary growth. Hence, when the time available for crystallization decreases the average crystallinity in

Fig. 5. Summary of the peak fitting process of the excess heat capacity during cooling in the scan rates investigated for DSC and FSC.

Fig. 6. Deconvoluted crystallinity versus temperature at 200 °C/s (a) and final crystallinity fractions for all cooling rates investigated (b).

each spherulite will reduce. The drop in the total crystallinity is outside the reach of both our DSC and FSC setup (between 10^0 and 10^1 °C/s). Only at very high cooling rates a minor decrease of the primary crystallinity is noted. For many semi-crystalline polymers it is possible to obtain a fully amorphous material by rapid cooling the sample from the melt at a critical cooling rate, $\dot{T}_{crit}$. Currently, to the best knowledge of the authors, this is not yet reported for m-LLDPE. From the data plotted here, $\dot{T}_{crit}$ is estimated to be in the order of 10^6 °C/s.

The maximum crystallinity for each fraction, χ_i , was determined from the same figure, see Table 1, and used in our modeling section later on.

3.2. Small-angle light scattering

Light scattering of semi-crystalline polymers has been studied for an extensive amount of time and is commonly used to extract morphological details from polymers [43,49–51]. The method was first applied by Debye and Bueche [52], and later on more detailed and complex theories were developed for polarized light scattering of common polymer morphologies such as single spherulites [32,53,54] and solid films with space-filling architectures [55]. Scattering in H_v mode is dependent on the size and anisotropy of the spherulitic entities. As a result, spherulitic growth can be detected by the changing scattering pattern and quantified from the integrated 2D scattering patterns. When it is assumed that only perfect spherulitic structures are formed, the average radius of the spherulites, R_{av} , can be determined by tracing the scattering vector with maximum intensity, q_{max} , in time using [56]:

$$R_{av} = \frac{4.09\lambda_0}{4\pi n_m \sin(\theta_{max}/2)} \approx \frac{4.09}{q_{max}} \quad (1)$$

wherein λ_0 is the wavelength of light in vacuum, θ the radial scattering angle and n_m the refractive index of the medium. In order to successfully investigate rapidly crystallizing polymers under (approximately) isothermal conditions, the challenge is to reach the desired temperature before any significant amount of crystallization takes place. In this work, the temperature jump-stage allows us to study crystallization of m-LLDPE up to high levels of undercooling, although no real-time measure for the actual sample

temperature can be provided, such as in the setup of Ding and Sprueill [57,58]. Reaching real isothermal conditions becomes critical for relatively high undercoolings and corrections might be required. We will discuss this issue in detail in the next section. The obtained time evolution of radii is displayed for three different temperatures only in order not to crowd Fig. 7. These data were selected to provide an overview of the measurements in the temperature range investigated. Data is shifted in time with t_0 , which represents the experimental time at which a clear peak in the scattering pattern was obtained.

When a sufficient amount of scattering is recorded as a result of space filling spherulites, q_{max} can be determined accurately. Consequently, only the final part of linear growth and subsequent impingement is detected. Nevertheless, a first order function can be fit to the data to obtain the temperature dependent spherulitic growth rate, $G(T)$. The average growth rate is plotted for all experiments in Fig. 8a and shows the characteristic bell shaped curve as commonly observed for various semi-crystalline polymers [59]. An apparent maximum growth rate is measured at ~78 °C of approximately 3 $\mu\text{m/s}$. Although the temperature at the maximum growth rate is in agreement with earlier findings [58], the growth rate is much lower compared to values for ethylene copolymers reported in literature [60].

The temperature dependent heterogeneous nucleation density, $N(T)$, plotted in Fig. 8b, was estimated from the final radius measured using [20,21]:

Fig. 7. Average spherulitic radius versus time for three different temperatures measured using SALS. Dashed lines indicate the linear growth rate.

Table 1

Maximum crystallinity content for the primary-, lamellar insertion-, bundle-like fractions, and total crystallinity, respectively.

	χ_{∞}^p	χ_{∞}^l	χ_{∞}^b	χ_{∞}^t
[-]	0.152	0.2015	0.103	0.457

Fig. 8. Spherulitic growth rate (a) and nucleation density (b) versus temperature measuring using SALS. Dashed lines indicate the least squares approximation of Eqs. (4) and (5), respectively.

$$\xi = 1 - \exp\left(-\frac{4}{3}\pi R^3 N\right), \quad (2)$$

which, at space filling, ξ , of 50% can be rewritten using the final spherulite radius, R_f ,

$$N = \frac{-\ln\left(\frac{1}{2}\right)}{\frac{4}{3}\pi R_f^3} \quad (3)$$

and shows the usual logarithmic decrease of the number of spherulites with temperature [61]. Temperature dependent functions for $G(T)$ and $N(T)$ can be obtained via least-square approximation of the measurements using:

$$G(T) = G_{max} \exp\left(-c_g(T(t) - T_{Gref})^2\right), \quad (4)$$

$$N(T) = N_{ref} \exp\left(-c_n(T(t) - T_{Nref})\right). \quad (5)$$

where G_{max} and N_{ref} are values at the reference temperatures T_{Gref} and T_{Nref} , respectively, while both c_g and c_n are constants. Good fits are obtained and included in Fig. 8.

Next to the average size and number of the spherulites, SALS can also provide details about the type of crystal growth measured, therefore, the relative invariant, Q , the total integrated scatter intensity of the H_v patterns, is employed:

$$Q = \int_0^\infty I(q) q^2 dq. \quad (6)$$

Subsequently, Q is normalized with respect to the first frame (fully amorphous sample, 0) and final frame (fully crystalline sample, 1). The invariant is proportional to the mean square anisotropy within the spherulites, and increases linearly with space filling [43] in Fig. 9a. The increase of Q after spherulitic impingement is an indication of an increased crystallinity or ordering degree within the spherulites as a result of secondary crystallization. Avrami analyses in Fig. 9b confirms that, after start up phenomena, crystallization occurs via spherulitic growth (slope close to 3) and a considerable amount of secondary crystallization (slope close to 1) via one dimensional growth such as lamellar insertion.

3.3. Primary crystallization model

The non-isothermal primary crystallization kinetics are calculated using the Schneider rate equations [62], a generalized form of the well-known Avrami analysis [20,21] that accounts for the effects of changing temperature during crystallization. This approach has been validated in a number of publications, cf. refs. [41,63]. The evolution of space filling is obtained by solving a set of coupled differential equations to calculate the evolution of radius density, area density, and undisturbed volume fraction for spherulites from number density and crystal growth rate. These equations read

$$\dot{\phi}_3 = 8\pi\dot{N} \quad (\phi_3 = 8\pi N), \quad (7)$$

$$\dot{\phi}_2 = G\phi_3 \quad (\phi_2 = 8\pi R_{tot}), \quad (8)$$

$$\dot{\phi}_1 = G\phi_2 \quad (\phi_1 = S_{tot}), \quad (9)$$

$$\dot{\phi}_0 = G\phi_1 \quad (\phi_0 = V_{tot}). \quad (10)$$

Here G denotes the spherulitic crystal growth rate and N the nucleation density, given as a function of temperature in Eqs. (4) and (5), respectively. Finally, space filling is calculated from the undisturbed volume fraction, ϕ_0 , using [20,21].

$$\dot{\xi}_p(t) = (1 - \xi_p(t))\dot{\phi}_0(t). \quad (11)$$

wherein

$$\xi_p(t) = \frac{\chi_p(t)}{\chi_\infty^p}. \quad (12)$$

Fig. 10 shows the primary crystallinity obtained from calorimetry and the crystallinity calculated from the FSC and DSC temperature profiles and the $G(T)$ and $N(T)$ from SALS measurements by the methodology described above. Upon immediate notice, it becomes clear that only the experiments from DSC are described accordingly. Here, independent of the cooling rates used, crystallization always takes place at approximately 100 °C, thus, only the SALS data obtained at low levels of undercooling describe the data well. For the high cooling rates, the calculated crystallization rate is too low and, consequently, the final primary crystallinity level is as well. In the next section, we analyze the SALS results in more detail to evaluate the measurement data at higher undercooling.

Fig. 9. Normalized relative invariant versus time at three different temperatures (a) and corresponding Avrami plot (b).

Fig. 10. Primary crystallinity from calorimetry experiments versus temperature (a) and time (b). Dashed lines are the computed values with crystallization kinetics from SALS.

3.3.1. Temperature correction calculations

The design of the jump stage is such that the cooling rate of the support can be considered infinite. The polymer sample however will not reach the set temperature instantaneously. For low set temperatures this will lead to a discrepancy between the set temperature and the temperature at which crystallization takes place. To account for this, the transient temperature in the sample needs to be determined [64]. Calculations were performed by solving the heat balance (using a built-in ordinary differential equation solver in matlab) on a 1D finite difference grid representing the experimental setup in Fig. 11.

The heat balance is given by

$$\rho^k c_p^k \frac{\partial T}{\partial t} = \lambda^k \frac{\partial^2 T}{\partial x^2} + \rho^k \chi_\infty \Delta H \dot{\xi}, \tag{13}$$

with T the temperature and t time. Further, ρ denotes density, c_p is the heat capacity, and λ is the thermal conductivity. Superscript k

denotes the material; either silver (heating element), glass (sample cover), or polymer. Values are given in Table 2. The last term in the right hand side represents the heat release due to crystallization of the polymer, with $\Delta H(T)$ the heat of fusion [47], χ_∞ the final crystallinity of the material and $\dot{\xi}$ the crystallization rate as given by the Schneider rate equations, including the obtained functions for nucleation density and growth rate. We assume that the maximum reachable crystallinity in this temperature range consists of crystals grown during the primary and lamellar insertion process, from Table 1 we obtain $\chi_\infty^p + \chi_\infty^l = 0.35$.

The crystallization temperature is defined as the temperature at which space filling in the center of the polymer sample reaches 70%, which is similar to the crystallinity level at which the linear growth rate was determined in SALS analyses. In Fig. 12 we present the results of this exercise. Fig. 12a shows the calculated crystallization temperature versus the set temperature for the originally measured data. The dashed line shows the case where these would be equal. The corresponding temperature transients in the center of the polymer sample are presented in Fig. 12b. Clearly, the crystallization temperature start to deviate from the set temperature from 92 °C downwards.

Table 2
Parameters for energy balance [65].

	Silver	Glass	Polyethylene
ρ [10^3 kg/m ³]	10.5	2.5	0.76
c_p [J/kg K]	233	0.5	3000
λ [W/mK]	429	1.05	0.23

Fig. 11. Cross section and dimensions of the sample and the temperature jump stage located in the SALS setup.

Fig. 12. Results of the heat balance calculations. (a) The calculated crystallization temperature versus the set stage temperature for measured data and corrected data (next section) and (b) the heat traces in the center of the polymer sample.

If the calculated temperature shift, $\delta T(T)$, is implemented as a correction to the SALS results, only part of the data will shift to higher temperatures, while both the growth rate and nucleation density values are maintained. Consequently, the functions determined in Eqs. (4) and (5) have to be re-evaluated.

Since δT is a function of the crystallization rate, thus of the measurement points themselves, see Eq. (13), a different approach is needed to calculate the correct material functions for N and G . From Fig. 12a, it becomes clear δT is not significant for measurements above 90 °C (<1 °C). Thus, these points can be used in the corrected least-squares approximation of the nucleation density, $N^*(T)$. This number of data points is insufficient to determine a corrected bell-shaped growth rate function, $G^*(T)$. Instead, G^* was obtained by least-square optimization of the calculated primary crystallization fraction from calorimetry, wherein N^* is included for calculations. As expected, an excellent description of the primary crystallinity content is obtained in a range exceeding five decades in time, see Fig. 13b. Parameter values obtained are displayed in Table 3 for both the original and corrected functions.

When the obtained growth rate function is verified, it becomes apparent that at lower temperatures, e.g. below 90 °C, G^* strongly deviates from G and a much higher maximum growth rate value is obtained, which ensures a significant crystallization rate even at low temperatures. The values of G_{max} and T_{Gref} show good agreement with literature [58,60]. When G^* and N^* are implemented in Eq. (13) and δT is again calculated, both shifted measurement data for N and G correspond with both G^* and N^* , see Fig. 14. Data above 90 °C still shows a neglectable δT and overlaps the set temperature

Table 3

Parameters for nucleation and growth functions. Values for functions marked with * are obtained after temperature correction.

	$G(T)$	$G^*(T)$
G_{max} [m/s]	$1.897 \cdot 10^{-6}$	$5.548 \cdot 10^{-5}$
c_g [1/K ²]	$7.1 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$
T_{Gref} [K]	349.5	336.5
	$N(T)$	$N^*(T)$
N_{max} [1/m ³]	$1.349 \cdot 10^{17}$	$1.257 \cdot 10^{17}$
c_n [1/K]	$4.60 \cdot 10^{-2}$	$7.24 \cdot 10^{-2}$
T_{Nref} [K]	383	383

during the SALS measurements, see also Fig. 12a. This confirms the accuracy of our calibration and analyses methods to calculate the growth rate and nucleation density, but simultaneously shows the SALS setup cannot be used for this material below 90 °C without additional heat balance calculations. The sample dimensions required do not allow for a micro-thermocouple to be included, for example, in between the two glass sample covers.

3.4. Secondary crystallization model

The total crystallinity fraction, including the increase of crystallinity due to secondary crystallization, can be expressed in terms of a convolution integral [23,25]:

Fig. 13. Primary crystallinity from calorimetry experiments versus temperature (a) and time (b). Dashed lines are the computed values with the temperature corrected function for nucleation and growth.

Fig. 14. Original and temperature corrected growth rate (a) and nucleation density (b) versus temperature.

$$\chi(t) = \int_{\tau=0}^t \dot{\xi}(t-\tau) \chi_{\infty}(t) d\tau, \quad (14)$$

where χ_{∞} is the maximum value of crystallinity allowed by the external conditions experienced by the sample [66]. If each spherulite has an initial (primary) crystallinity equal to χ_{∞}^p , the evolution of the maximum crystallinity during solidification yields:

$$\chi_{\infty}(t) = \int_{\tau}^t \dot{\chi}_{\infty}(T(t)) dt + \chi_{\infty}^p. \quad (15)$$

Here, the increase of the maximum crystallinity, $\dot{\chi}_{\infty}$, can be expressed as a strong function of the environmental conditions, e.g. temperature, and the current amount of remaining amorphous material using, similar to Eq. (11):

$$\dot{\chi}_{\infty}(T(t)) = \sum \left(1 - \xi_{\infty}^i\right)^{n_i} K_i(T), \quad (16)$$

wherein n_i is an Avrami-like diffusion constant that provides a strong dependence on the current amount of amorphous material,

$$\xi_{\infty}^i = \frac{\chi_i(t)}{\chi_{\infty}^i} \quad (17)$$

where i denotes the multiple secondary crystallization processes and

$$K_i(T) = a_i \exp \left(-b_i \frac{(T - T_{ref,i})^2}{T^2} \right), \quad (18)$$

is introduced as a temperature dependent rate function with constants a_i , b_i and $T_{ref,i}$. Their context is briefly discussed. The reference temperature, $T_{ref,i}$, corresponds to the temperature of maximum rate, a_i , of secondary structure formation. The value for b_i governs the width of the function, i.e. determines the temperature range in which secondary morphologies are able to form. Subscripts l and b are used for lamellar insertion and formation of bundle-like structures, respectively. The maximum crystallinity values for each process, χ_{∞}^i , in Eq. (17) are obtained from calorimetric analysis and were provided earlier in Table 1.

By employing the convolution integral approach, nucleated spherulites that have grown for a longer period in time, i.e. those that are formed at higher temperatures, will contain a higher

amount of secondary crystallinity. The contributions of both the lamellar insertion and bundle-like ordering process were determined versus time and temperature from calorimetry. With the primary process described accurately, parameters for the rate functions can be determined. Typical initial values for this process could be estimated from the calorimetry results. Results of applying this model are shown in Fig. 15 and parameter values are summarized in Table 4. The model is able to describe the multiple crystallization processes well, especially for conventional DSC data. Here, the onset of the lamellar insertion process starts already during the fast primary space filling process. Also the inflection point that marks the bundle-like ordering is captured well. Regarding the FSC experiments, good agreement is obtained in most cases. The final crystallinity level decreases with cooling rate although the final values and secondary processes are not always described accurately.

Parameters for the rate functions are shown in Table 4, both rate functions are displayed in Fig. 16. The reference temperature, $T_{ref,i}$, is lower for the bundle-like process, coherent with calorimetry measurements, clearly this process is dominant at low temperatures (<60 °C). The maximum rate, a_i , is found to be orders of magnitude higher for the bundle-like process; the scaling parameter, n_b in Eq. (16), provides the secondary crystallization rate with a strong dependency on the remaining crystallizable amount of amorphous material, consequently, a_b is relatively large.

3.5. Extended dilatometry

Using the Pirouette, the influence of the thermomechanical history during cooling was investigated by applying flow as a step function of one second in a range of shear rates, similar to cf. refs. [26,67]. The shear temperature, $T_{\dot{\gamma}}$, was chosen such that the undercooling, $\Delta T(p)$, was 0 and 5 °C by taking into account the pressure corrected melting temperature, $T_m(p)$. This level of undercooling was chosen such that we get clear but not too strong effects of the flow applied. $T_{\dot{\gamma}}$ is defined as:

$$T_{\dot{\gamma}} = T_m(p_0) + \kappa(p - p_0) - \Delta T, \quad (19)$$

where κ is the pressure shift factor taken at 27.5 °C/kbar as generally accepted for polyolefins [68], p_0 the atmospheric pressure in bar and ΔT the level of undercooling.

The melting temperature at atmospheric conditions was determined from standard DSC at 114.3 °C, see Appendix B. The investigated shear temperatures are summarized for each pressure in Table 5.

To easily compare the influence of different thermomechanical

Fig. 15. Total crystallinity from calorimetry experiments versus temperature (a) and time (b). Dashed lines are the computed values with the model for primary and secondary crystallization.

Table 4

Constants for each secondary crystallization process in Eqs. (16) and (18).

	K_i	K_b
a_i [1/s]	0.485	$1.034 \cdot 10^3$
b_i [-]	963.78	817.02
$T_{ref,i}$ [K]	339.6	297.6
n_i [-]	3.32	8.45

Fig. 16. Rate function, K_i , of both secondary crystallization processes versus temperature.

Table 5

Shear temperature during dilatometry experiments at both pressures investigated.

	$\Delta T = 0$	$\Delta T = 5$
100 [bar]	117 °C	112 °C
500 [bar]	128 °C	123 °C

histories on the crystallization process, rather than to focus on the absolute value of the specific volume, the raw data is converted in a normalized specific volume, ν^* , using:

$$\nu^* = \frac{\nu - \nu_s}{\nu_m - \nu_s}, \quad (20)$$

where ν is the measured specific volume, ν_s the specific volume in

the solid state at 40 °C and ν_m the specific volume in the melt at 170 °C.

Results are plotted in Fig. 17. The dilatometry curves consists of three different regions, the melt, crystallization and solid regime, from high to low temperatures, respectively. The 'dip' in the experimental data is caused by the shear pulse and cannot be avoided. In the case of 100 bar and $\Delta T = 0$ (Fig. 17a), hardly any influence of flow is noticeable; the volume contraction associated to crystallization always begins at the same temperature and proceeds in the same temperature range. The major decrease of the specific volume originates from the primary crystallization process at ~ 100 °C, in addition, a weak effect of second stage secondary crystallization is noted at ~ 70 °C. Experiments at an equivalent pressure level with a reduced shear temperature, $\Delta T = 5$ (Fig. 17b), show a clear influence of flow; the crystallization temperature increases a maximum of approximately 10 °C. For strong enough flow, the material partially crystallizes during the shear pulse. As a result of the applied shear, the molecules become arranged in flow direction, decreasing the melt entropy, thus increasing the driving force for crystallization. Molecular orientation stimulates the formation of flow induced nuclei, which, depending on the conditions, can tremendously increase the rate of crystallization [61]. More pronounced effects of flow are found when the level of undercooling is kept constant and, at the same time, the pressure is increased (Fig. 17c,d). At elevated pressure, the nucleation barrier is reduced since the molecules are packed more closely together, inducing an enhanced crystallization rate with flow [26,59]. Weak signs of a secondary crystallization process are found at 80 °C (a temperature shift of ~ 10 °C with respect to the measurements at 100 bar due to the pressure difference). Fig. 17d, containing the conditions at slightly higher undercooling, shows a vast influence of flow; crystallization sets in during or immediately after the shear pulse.

To distil the effect of shear on the different crystallization processes, i.e. primary and secondary crystallization, the first derivative of the normalized specific volume, $(\delta \nu^* / \delta T)$, is plotted versus temperature, which amplifies any change in curvature. A signal closely representing the calorimetry measurements (see Fig. 5), but now with the influence of pressure and flow, is obtained in Fig. 18. Notice that, by presenting the PVT-results in this way, we have a DSC-equivalent signal that includes the influence of high pressure (upto 1200 bar) and, and this is unique, the influence of high shear rates (upto 180 1/s). Indeed, the signal originating from latent heat release and the rate of density change both scale with the crystallization rate. Under isobaric conditions, the specific volume drop during cooling is nearly linear at high temperature because the

Fig. 17. Normalized specific volume versus temperature for dilatometry experiments with flow at different shear temperatures at 100 bar (a,b) and 500 bar (c,d).

Fig. 18. Derivative of the specific volume versus temperature from dilatometry experiments with flow at different shear temperatures at 100 bar (a,b) and 500 bar (c,d).

thermal expansion coefficient of the melt is only weakly a function of temperature. Similar to results from calorimetry, we can recognize the peak as a result of primary crystallization, which becomes asymmetric at lower temperatures because of the lamellar insertion process. Finally, at even lower temperatures, bundle-like crystallization is observed with a smaller, but clearly distinguishable peak. For the experiments with shear, a large spike in the derivative was obtained originating from the shear pulse. In order to present a clear figure, $(\delta\nu^*/\delta T)$ is plotted only from the moment directly after the shear pulse. For mild shear conditions, the derivative starts below the linear melt level because of the ‘recovery’ time needed after shear. In the case crystallization occurs during the one second shear pulse, the first part of the derivative is found above the linear melt level and during the primary crystallization peak. Regarding Fig. 18b–d, the experimental conditions with a clear effect of flow, primary crystallization shifts towards higher temperatures. Here, flow increases the amount of point-like nuclei or induces the formation of oriented structures (shish), thus, the primary space filling process is enhanced. Compared to Fig. 17, the effect of flow on the bundle-like crystallization process is now much more clear, evidently, the magnitude reduces with shear rate. With an increasing level of molecular orientation, the segmental motion of the side chains becomes constrained, moreover, the molecules are stretched in flow direction, providing that the side chains gradually become distanced from each other and can no longer form local crystalline aggregates.

3.5.1. Flow strength: the Weissenberg number

The influence of the different processing histories applied is usually captured by converting the experienced thermomechanical history into a single parameter. A dimensionless shear rate number, i.e. the Weissenberg number, Wi , is commonly used to express the strength of flow applied and, simultaneously, proved to be useful for a rheological classification of the resulting type of crystalline morphology [67,69,70]. For low Wi -numbers, no clear effect on the crystallization kinetics is expected. For strong enough flow, part of the molecular chains (those with the higher molecular weight) become sufficiently stretched and oriented creating extra nuclei (flow enhanced nucleation), while the growth rate and growth-mechanism remain unaffected. At even higher Wi numbers, high amounts of shear induced nuclei are generated and oriented crystalline structures are formed and even the growth rate might be influenced [71]. Transitions between the different flow-induced crystallization regimes are defined by critical values of the Wi -number [69,70]. As the influence of flow is thought to work via molecular stretch [69,72], the Weissenberg number is defined as:

$$Wi = a_T a_P \tau_R \dot{\gamma}, \quad (21)$$

where $\dot{\gamma}$ is the applied shear rate and τ_R the characteristic rheological stretch relaxation time of the high molecular weight tail. The stretch relaxation time is obtained from fitting the model parameters for the XPP model [73], describing non-linear viscoelastic flow behavior, to viscosity data in uniaxial extension (see Appendix C), resulting in $\tau_R = 16.2$ s at a reference temperature of 160 °C and pressure of 1 bar. The temperature shift factor, a_T , is described with an Arrhenius type equation:

$$a_T = \exp\left(-c_1 \left(\frac{T_{ref} - T}{T_{ref} T}\right)\right), \quad (22)$$

with T the absolute temperature, T_{ref} a reference temperature of 160 °C and c_1 a constant. Values were obtained by time–temperature superposition of linear rheological data, also included in Appendix C. The pressure shift factor a_P is defined as [74]:

$$a_P = \exp\left(\kappa(p - p_{ref})\right), \quad (23)$$

where κ is $14 \cdot 10^{-9} \text{ P}^{-1}$ for a relatively similar LLPDE grade [15] and p_{ref} a reference pressure of 1 bar. Note that, in this study, the relaxation times calculated by the XPP model were adopted, resulting in rather high Wi numbers.

Similar to Van der Beek et al. [67] a dimensionless crystallization temperature θ is used to express the change in crystallization kinetics measured:

$$\theta = \frac{T_c^{\dot{\gamma}}}{T_c^Q}, \quad (24)$$

where $T_c^{\dot{\gamma}}$ and T_c^Q are the peak temperature of primary crystallization with shear and during quiescent crystallization, respectively (see Fig. 18). In Fig. 19, θ is plotted versus Wi . From this figure, we can distinguish between no influence of flow, mild influence and strong influence. In van Erp et al. [75], similar experimental results for an iPP grade are presented. They also observed the three different influences of the flow strength, but this resulted in three clearly separated regimes, i.e. for a given Wi -number there was (within experimental error) one dimensionless crystallization temperature only. Here, no such clear trend is observed; for the same Wi -number different transition temperatures are found depending on the thermomechanical history. It can be appreciated from the 2D WAXD figures included in Fig. 19, obtained for the four samples processed at highest shear rate of 180 1/s, that a notable difference exists in final molecular orientation. For the sample processed at 100 bar and $\Delta T = 0$, a slightly polarized pattern is obtained, indicating the growth of flow-enhanced and/or oriented spherulites. For the other shear conditions, clearly a heavily oriented sample morphology was obtained after the imposed thermomechanical history. This apparent problem will be clarified in the next section where we present a model that captures these flow induced crystallization phenomena.

3.6. Flow-induced primary crystallization model

A brief description is given of the FIC model developed in the Peters group [26,72,76,77], the reader is referred to literature for an

Fig. 19. Dimensionless crystallization temperature versus Weissenberg number; experimental results, and 2D WAXD pattern of the samples at the highest shear rates investigated (shear direction is vertical).

in-depth evaluation. The model couples nucleation rate and formation of oriented structures to a qualitative predictive rheological model. It is stressed that the modeling section is assumed to apply to flow-induced primary crystallization only. Scaling parameters are determined to describe the obtained flow-enhanced crystallization kinetics as measured in the previous section (see Fig. 19).

With flow, the total number of nuclei is considered the sum of quiescent nuclei, N_Q (Eq. (5)), and nuclei originating from flow-induced crystallization, N_f :

$$N_{tot} = N_Q + N_f, \quad (25)$$

which is implemented in Eq. (7). The flow enhanced nucleation rate is modeled using a fourth-order dependence on the backbone stretch of the molecules in the high molecular weight (HMW) tail of the material, similar to [72]. It is envisioned that the stretch of the longest chains increases the number of aligned chain segments whose conformation is closer to the crystalline state

$$\dot{N}_f = g_n (\Lambda_{HMW}^4 - 1) \quad (26)$$

wherein $g_n = g_n(T, p)$ is a temperature and pressure dependent scaling parameter.

The constitutive behavior on a molecular level is calculated using the XPP model [73]. The relaxation times of the chains, τ_i , are corrected for shear-temperature and pressure. In addition, the flow-induced nuclei are assumed to act as physical crosslinks in the melt, increasing the relaxation times of the high molecular weight chains which is implemented with a linear dependency [77]:

$$\tau_i = a_T a_p \tau_{i0} (1 + \alpha N_f) \quad (27)$$

in which a_T and a_p are the temperature and pressure shift factors, respectively. The value of α is assumed at 10^{-18} for the m-LLDPE used.

The growth of oriented structures (shish) is assumed to be a non-selective process, in which all chains in the melt, regardless of their molecular weight, can participate. The average (AVG) conformation of the chains, in terms of orientation and stretch, is assumed to control the growth rate of the shish. The shish growth rate is given by:

$$\dot{L} = g_l (\Lambda_{AVG}^4 - 1) \quad (28)$$

in which $g_l = g_l(T, p)$ is a scaling parameter dependent on both temperature and pressure.

A threshold flow condition needs to be surpassed before the length growth mechanism is activated and, consequently, oriented structures will form. Different criteria are suggested in literature; a critical shear rate, a critical amount of work, and a critical value for the stretch related to the high molecular weight tail (HMW-tail) of the molecular weight distribution. Here, similar to ref. [26], the time integral over the HMW-tail stretch history is used, a so-called effective stretch time:

$$t_{eff} = \int_0^t \Lambda_{HMW} dt \quad (29)$$

This rather simple criterium proved to work quite well for iPP [26] and, therefore, we will test if this is also the case for the m-LLDPE grade at hand. Notice that this criterium is similar (not the same) to a critical work criterium. Work reflects the average history of the deformation of all molecules, our criterium concerns the

deformation history of the HMW-tail molecules only. The fibrillar growth mechanism is activated only if a critical value of the stretch history is surpassed.

The undisturbed volume can be calculated in time from the calculated nucleation density and shish length. In the isotropic case, i.e. below the critical stretch level, Eqs. (7)–(10) are combined with Eq. (25). For the case of an oriented system, a similar set of rate equations, first proposed by Eder [61], is employed:

$$\dot{\psi}_3 = 8\pi \dot{N}_f \quad (\dot{\psi}_3 = 8\pi \dot{N}_f), \quad (30)$$

$$\dot{\psi}_2 = 4\pi \dot{N}_f \dot{L} \quad (\dot{\psi}_2 = 4\pi \dot{L}_{tot}), \quad (31)$$

$$\dot{\psi}_1 = G \psi_2 \quad (\dot{\psi}_1 = S_{tot}), \quad (32)$$

$$\dot{\psi}_0 = G \psi_1 \quad (\dot{\psi}_0 = V_{tot}) \quad (33)$$

with the nucleation rate $\dot{N}$, shish growth rate $\dot{L}$ and the spherulitic growth rate G . The morphology is described per unit volume by the total volume of shish-kebabs V_{tot} , their total surface S_{tot} , the sum of their lengths L_{tot} and the number of flow-induced nuclei N_f . Finally, the undisturbed spherulitic and oriented crystalline volume, ϕ_0 and ψ_0 , respectively, are included in the Avrami model for space filling:

$$\dot{\xi}_p(t) = (1 - \xi_p(t)) (\dot{\phi}_0(t) + \dot{\psi}_0(t)) \quad (34)$$

For each dilatometry experiment, the crystallization kinetics were calculated from the time, temperature, pressure and flow history recorded and the framework presented above. The experimental data is used to determine values for the scaling parameters included in Eqs. (26) and (28) and the critical effective stretch time, t_{crit} , from Eq. (29). The calculated effective stretch time is plotted versus the experimental dimensionless transition temperature in Fig. 20. The steep increase in θ is used to define t_{crit} , thus, from this value onwards, crystallization occurs via growth of shish-kebab structures. Data below t_{crit} covers either no influence of flow, or the enhanced point-like nucleation regime, and is used to determine values for scaling parameter g_n . Subsequently, data with an effective stretch time equal to or above the t_{crit} (and, simultaneously $\theta > 1.0075$, the flow regimes are really in two different quadrants, as it should be, see also [26]), is described using g_l . A

Fig. 20. Integral over the stretch history versus the experimental dimensionless crystallization temperature.

small number of experiments, during which crystallization was already observed during the shear pulse (150 and 180 1/s at $\Delta T = 5$ for 100 bar and 500 bar, respectively) are not included. These experimental conditions will be discussed separately.

Both the experimental and computed transition temperature are presented in Fig. 21. The different transition temperatures at equal Wi-numbers are well captured by the model, which confirms the competence of the chosen critical stretch criterium, governing the onset of flow-induced structures. Unexpectedly, the experiments at 100 bar and $\Delta T = 5$ show a slightly higher transition temperature compared to the 500 bar and $\Delta T = 5$ experiments, while the Wi-number is slightly higher in the case of 500 bar experiments. This could have also been observed from the experimental data alone, Fig. 19, but is more clear with the model predictions included. At first thought, the increased pressure level and shear pulse at equal undercooling should provide the polymer melt with a more severe thermomechanical history. From both the measurements and model calculations, it can be deduced that the effect of undercooling on the relaxation times (via a_T) exceeds the effect of pressure (via a_p).

The optimal scaling parameters and critical stretch time are displayed in Table 6. For a sufficient number of experiments, i.e. temperatures, pressures and shear rates, one could chose simple expressions that then capture the parameter spaces of $g_n(T,p)$ and $g_l(T,p)$, see Ref. [26]. However, due to the limited number of pressure/temperature combinations (4), we provided parameter values only.

Finally, the PVT experiments that showed pronounced crystallization during the shear pulse, and were excluded from our previous analyses, are briefly considered. The parameter values as given in Table 6 were used to predict the transition temperatures for the experiments at 100 and 500 bar and $\Delta T = 5$, i.e. the four measurements with the highest transition temperature. It can be appreciated from Fig. 21, that the obtained model values for the transition temperature are much lower compared to our obtained experimental values. If we consider the occurrence of crystal growth during shear as a tremendous increase of the number of physical crosslinks, the measured transition temperatures can be approached by altering the α parameter, i.e. the dependency of the relaxation time on the number of flow-induced nuclei (Eq. (27)). If α is chosen at $1 \cdot 10^{-11}$, relaxation times of the stretched molecules are increased, introducing extremely short crystallization times and/or crystallization during the shear pulse is approached, see Fig. 22.

Fig. 21. Dimensionless crystallization temperature versus Weissenberg number. Open symbols represent the experiments, closed symbols results from the model, respectively.

Table 6

Optimized values for flow-induced (scaling) parameters.

	$g_n [m^{-3} s^{-1}]$	$g_l [m s^{-1}]$
100 bar, $\Delta T = 0$	$2.1 \cdot 10^{13}$	n/a
100 bar, $\Delta T = 5$	$6.0 \cdot 10^{13}$	$9.1 \cdot 10^{-6}$
500 bar, $\Delta T = 0$	$1.6 \cdot 10^{13}$	$7.6 \cdot 10^{-6}$
500 bar, $\Delta T = 5$	$6.3 \cdot 10^{13}$	$8.1 \cdot 10^{-6}$
t_{crit}	54.3 [s]	
α	$1 \cdot 10^{-18} [m^3]$	

4. Conclusion

In this work, an extensive characterization of the crystallization kinetics of a m-LLDPE grade is shown as function of cooling rate, flow strength and pressure. A peak decomposition process is applied to distinguish between the different crystallization processes observed in (fast-) differential scanning calorimetry, i.e. primary and two secondary crystallization processes. It was observed that with cooling rate, mainly the lamellar insertion process is suppressed, lowering the final crystallinity of the sample. The most important material functions to describe quiescent crystallization, the temperature dependent nucleation density and spherulitic growth rate, were obtained from SALS measurements accompanied with heat-balance calculations.

The proposed model to describe non-isothermal crystallization includes a convolution integral approach to describe secondary crystallization, for which the parameters were determined from the experiments. The model shows an accurate description of the crystallinity evolution in the range of cooling rates investigated (0.07–2000 °C/s).

Dilatometry is used to investigate the influence of flow strength and pressure and primary and secondary crystallization. It was shown that flow promotes primary crystallization, while the low-temperature bundle-like process is strongly reduced at the highest flow conditions. A simplified version of a molecular-based nucleation model is used to describe the primary crystallization kinetics as function of flow and thermal history. Application of this model allowed for optimization of the scaling parameters g_n and g_l to describe the rate of flow enhanced nucleation and shish growth, respectively. When the strength of flow is expressed as the dimensionless Weissenberg number, different transition temperatures are found depending on the thermomechanical history. These

Fig. 22. Dimensionless crystallization temperature versus Weissenberg number. Open symbols represent the experiments, closed symbols results from the model, respectively. A strong coupling between relaxation time and number of nuclei is included for the experiments where crystallization occurred during the shear pulse.

Fig. 23. Heat capacity versus temperature during heating.

Fig. 24. Storage (circles) and loss (squares) moduli at $T_{ref} = 160$ °C. Full lines represent the fitting obtained with a Maxwell spectrum.

Table 7

Rheological parameters for the material studied: Maxwell relaxation spectrum at 160 °C, g_i and τ_i . Time–temperature horizontal and vertical shift factors, a_T and b_T .

Modes	g_i [Pa]	τ_i [s]
1	$5.07 \cdot 10^5$	0.000774
2	$2.06 \cdot 10^5$	0.00581
3	$7.59 \cdot 10^4$	0.0356
4	$1.86 \cdot 10^4$	0.227
5	$5.57 \cdot 10^3$	1.53
6	$1.48 \cdot 10^3$	8.95
7	274	55.4
T [°C]	a_T	b_T
115	4.23	0.765
120	3.59	0.806
140	1.77	0.909
160	1	1
180	0.522	1.12
200	0.306	1.23

results show that, in the case of m-LLDPE, the Wi-number does not provide an unambiguous rheological classification of the type of crystallization process. Even though, the model is able to capture the measured crystallization kinetics, reasserting the applicability of the critical stretch criterium selected.

Fig. 25. Transient extensional viscosity for the m-LLDPE studied over a range of strain rates measured at melt temperatures of 160 °C. The dotted lines represent the linear viscoelastic behavior and the full lines the XPP model fit.

Table 8

Non linear XPP parameters for the material studied at 160 °C: stretch times, λ_i , and number of arms, q_i .

Modes	λ_i [s]	q_i [s]
1	$1 \cdot 10^{-6}$	1
2	$1 \cdot 10^{-6}$	1.98
3	1 10s	3.02
4	0.021	3.02
5	0.0441	3.06
6	2.29	3.06
7	16.2	3.63

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Appendix A

Temperature Rising Elution Fractionation (TREF) analysis was done using a CRYSTAF-TREF 200 + instrument from Polymer Char, S.A., Valencia, Spain. The principles of TREF analysis and a general description of the particular apparatus used are given in [79]. Details of the analysis method and features of the apparatus used are as follows. 1,2-Dichlorobenzene (ODCB) solvent stabilized with approximately 380 ppm of 2,6-bis(1,1-dimethylethyl)-4-methylphenol (butylated hydroxytoluene) was used for preparing the sample solution and for elution. The sample to be analyzed (100.0 mg) was dissolved in ODCB (25 ml metered at ambient temperature) by discontinuous stirring (200/200 rpm, High/Low; 300/5 s, On/Off) at 150 °C for 60 min. A small volume (0.5 ml) of the solution was introduced into a column (15-cm long by 3/8 o.d.) packed with an inert support (stainless-steel balls) at 150 °C, and the column temperature was stabilized at 140 °C for 45 min. The sample volume was then allowed to crystallize in the column by reducing the temperature to 30 °C at a cooling rate of 1 °C/min. The column was kept at 30 °C for 15 min before injecting the ODCB flow (1 ml/min) into the column for 10 min to elute and measure the polymer that did not crystallize (soluble fraction). The infrared detector used (Polymer Char IR4) generates an absorbance signal that is proportional to the concentration of polymer in the eluting flow. A complete TREF curve was then generated by increasing the temperature of the column from 30 to 140 °C at a rate of 2 °C/min while maintaining the ODCB flow at 1 ml/min to elute and measure the dissolving polymer.

Appendix B

The melting point at atmospheric pressure was determined at 114.3 °C from the peak in enthalpic heat from DSC at a heating rate of 10 °C/min. Data is plotted in Fig. 23.

Appendix C

The rheological properties at a temperature of 160 °C are shown in Fig. 24. An Arrhenius temperature dependence is found for the horizontal shift factors (a_T) and vertical shift factors (b_T) which are listed in Table 7, the latter, as expected did not show strong temperature dependence. The calculated value for the activation energy, E_a , is 47.686 kJ/mol.

The relaxation time spectrum of the polymer in the melt state (at 160 °C) can be calculated from the rheological properties measured. For that purpose, a discrete Maxwell relaxation time spectrum is used [78]. The set of relaxation moduli, g_i , and times, τ_i , are given in Table 7 which fit well the measured G' and G'' (solid lines in Fig. 24).

Transient uniaxial elongational viscosities, η_{II}^+ , at strain rates ranging from 0.1 to 25 1/s at 160 °C are given in Fig. 25. The dashed line represents the linear visco-elastic (LVE) behavior of transient elongational viscosity evaluated according to the Trouton-ratio, $\eta_{II}^+(t) = 3\eta_0^+(t)$ where $\eta_0^+(t)$ is the linear time-dependent shear viscosity evaluated from the relaxation spectrum at 160 °C. As typical for branched polymers deviation from linearity is observed: after a certain strain a positive stress deviation from the LVE envelope is noted (defined as strain hardening). The non-linearity was predicted using the XPP model [73]. Parameters q and the stretch time λ_s for the XPP model determined using the transient uniaxial viscosity are shown in Table 8, a Giesekus or α -parameter of $1/q_i$ was used.

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