Stress Induced Crystallization in Elongational Flow

Stress-induced crystallization is studied in an extensional flow device (a cross-slot flow cell) for an isotactic Polypropylene (iPP) by measuring the micro-structure that develops after flow. Birefringence and Wide Angle X-ray experiments were performed. The birefringence experiments with flow below the melting temperature showed the occurrence of a fiber-like structure around the outflow centerline and, later in time, of ‘streamlines’. The latter are explained by the influence of shear gradients close to the optical windows. The WAXS experiments performed. The birefringence experiments with flow above the melting temperature showed the occurrence of a fiber-like structure around the outflow centerline and, later in time, of ‘streamlines’. The latter are explained by the influence of shear gradients close to the optical windows. The WAXS experiments also showed the fiber-like structure around the outflow centerline, having orientations in the (110), (040) and (130) reflections, with a width of about 80 μm. This dominance of the elongational flow around the stagnation line could not be observed in experiments with flow above and subsequent crystallization below the melting temperature.

Structure development in this cell was numerically predicted using the Leonov and the extended Pompom (XPP) model. The oriented structures can be predicted. Moreover, process conditions are found with less influence of the (unwanted) shear gradients. Finally, it was concluded that the strain hardening behavior in the Leonov model over-estimates the first component of the Finger tensor, and thus the number of flow-induced nuclei. Therefore it is recommended to use the extended Pompom model as a more realistic basis for a quantitative flow-induced crystallization model.

1 Introduction

The properties of products made of semi-crystalline polymers depend on both, molecular properties and the processing conditions applied. Therefore in order to predict properties, a first step is to quantify the thermal-mechanical history experienced by the polymer in e.g. injection moulding, film blowing or fibre spinning. The next step is to model nucleation and crystallization kinetics and flow-induced structure formation.

Deformation influences the orientation of polymer chains and thus the resulting anisotropy of the crystals formed. Keller and Kolnaar [1] showed that fiber-like structures (shish) are created, beyond a critical elongational rate, orienting the high end tail of the molecular weight distribution with the largest configurational relaxation time. The lower molecular weight parts relax faster during and after deformation and crystallize as lamellae (kebab) nucleated by the fibers. Eder and Janeschitz-Kriegel [2] demonstrated that these structures are not only observed in (strong, irrotational) elongational flows, but also can be found in shear flows with high enough viscoelastic stresses. Shish-kebab structures were found in many polymer materials, like PE [1], iPP [2], PA6 [3] and PB [4]. They have an important influence on properties like warpage, anisotropic shrinkage, and even toughness (Schrauwen et al. [5]). Tas [6] observed that in the film blowing process, mechanical properties of different LDPE’s correlate surprisingly well with the viscoelastic stress at the crystallization line, much more than with macroscopic strain or strain rate, leading to the conclusion that chain orientation/extension is the governing phenomenon (see also Meijer [7]).

Chain extension can most easily be achieved in stagnation flows, see Schoonen [8] for an overview. Examples of these flows include the two roll mill, Frank and Mackley [9], Jeffroy and Leaf [10], the four roll mill, Crowley et al. [11], Dunlap and Leaf [12], McHugh et al. [13], the (lubricated) converging flow with a free stagnation point, van Aken and Janeschitz-Kriegel [14], Macosko et al. [15], the cross-slot device, Gardner et al. [16], Miles and Keller [17] and the opposed jets device, Janeschitz-Kriegel et al. [18], Keller et al. [19], Mackay et al. [20]. The basic principle of a stagnation flow is, in all cases, the same: two liquid streams are impinging. A free stagnation point is created in the center where the extensional strain can become very high.

In this study a cross-slot flow cell is used to investigate stress-induced crystallization in a melt (isotactic Polypropylene). The cell was designed to be operated in the in-situ X-ray facilities at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, and a numerical tool was developed to predict the resulting structure in this cell. The same geometry was also used by Gardner et al. [16], Miles and Keller [17], to investigate coil-stretch transitions in polymer solutions.

2 Measurement of Flow-induced Crystallization

Reviews on flow-induced crystallization can be found in Eder et al. [21], McHugh [22] and Tribout et al. [23]. Here, we will focus on measurements and limit the review to work of the last decennium. About eight different experimental devices were used to measure flow-induced nucleation and crystallization (see Table 1). Shear flow was generated with the fiber pull out device, between sliding plates, in slits, in the Multi Pass Rheometer (MPR) and in shear or stress controlled rheometers. The four roll mill was the only device in which (local) pure
elongation (i.e. $\dot{\varepsilon}$ = constant) was applied. The melt spinning apparatus and the contraction flow cell can be considered as complex flows with a combination of shear and elongation. Only the melt spinning and the MPR experiments can approach industrial processing conditions. Spinning speeds up to 8.3 m/s, Schultz et al. [3], and shear rates up to 2225 s$^{-1}$, Mackley et al. [24], were reported.

Liedauer et al. [25] were the first to find a quantitative relation between the morphology and a shear-induced crystallization model, see also Eder and Janeschitz-Kriegl [2], Jerschow and Janeschitz-Kriegl [26, 27]. Liedauer found three different regions over the thickness of the duct: oriented structures close to the wall, spherulites in the center and a fine grained layer in between. The temperature dependence of the critical shear rates at which the boundaries of the three different layers were found was not pronounced. According to Jerschow and Janeschitz-Kriegl [26], the structures in the fine grained layer were thread-like particles which were oriented perpendicular to flow direction. Jerschow speculated that this orientation could be due to the second normal stress difference. It was stated that if shear rate and shear time are sufficiently high, these structures will rotate into the flow direction.

Most references in Table 1 applied a short time shearing approach at low supercooling, where flow and crystallization temperature are the same. Melt spinning experiments and the experiments of Monasse [28] and Vleeshouwers and Meijer [29] are exceptions. In melt spinning a flow temperature of about forty degrees above the (non-equilibrium) melting temperature was applied. Flow temperatures in the work of Vleeshouwers on iPP were in between 200 and 260°C. Monasse used flow temperatures of 170 and 210°C for iPP. In these experiments relaxation can influence the occurrence of oriented structures, especially if the cooling rate is not large enough. Disadvantage of short time shearing at relatively low temperatures could, however, be the interaction of formed structures with flow. Crystalline structures can appear during flow. Kumaraswamy et al. [30] noticed an oriented WAXS pattern during the first 5 s of shearing. The peaks grew rapidly until 100 s, after which they saturate and grow relatively slowly. Mackley et al. [24] observed, after 10 s shearing of HDPE in the MPR at 135°C and 225 s$^{-1}$, an increase in pressure and formation of fibers. Typically, these oriented structures were not observed at a higher shear rate of 2250 s$^{-1}$. According to Mackley, slip at the wall suppressed crystallization at this high shear rate.

Secondary nucleation or growth was investigated in the fiber pull out device. Duplay et al. [31] investigated fourteen different polypropylene homopolymers, which differ in molecular weight and molecular weight distribution, but with the same tacticity. It was shown that sphercial growth of iPP is not influenced by molecular weight. Similar results were obtained by Eder et al. [21] and Galileiner et al. [32]. Magill [33] reported the opposite for poly(tetramethyl-p-silphenylene)-siloxane (TMPS), but the dependence became less for higher molecular weights. A decrease in growth rate with decreasing tacticity was shown by Galileiner et al. [32]. Duplay et al. [31] showed that the growth rate increased during shear and correlated with molecular weight. The largest deviation (ten times higher than in quiescent conditions) was found for a high molecular weight with a broad molecular weight distribution ($M_w = 375$ kg/mol

<table>
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<th>Method</th>
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<td>Tribout et al. [23]</td>
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<td>parallel plate: fiber pull out</td>
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Table 1. Studies on flow-induced nucleation and crystallization in alphabetical order

FB = Field-wise Birefringence, PB = Point-wise Birefringence, D = Dichroism, OM = Optical Microscopy, WAXS = Wide Angle X-ray Scattering, SAXS = Small Angle X-ray Scattering, TEM = Transmission Electron Microscopy, SAOS = Small Amplitude Oscillatory Shear, DTA = Differential Thermal Analysis, MPR = Multi Pass Rheometer, SFTR = Shear Flow Thermal Rheometer. PB 1 = Polybutene-1; HDPE = High Density Polyethylene; PA = Polyamide; iPP = isotactic Polypropylene; LMDPE = Linear Medium Density Polyethylene; PET = Poly(ethylene terephthalate); PVDF = poly(vinylidene fluoride); EPBC = Ethylene-Propylene Block Copolymer
and MWD = 3.2). Also Tribout et al. [23] showed a shear dependent growth rate. The growth rates during shear were about five times, and after shear about 1.5 times, higher than in static conditions, and increased linearly with increasing shear rate. Thus tacticity seems to be the most important molecular parameter on growth rate in quiescent conditions at a constant temperature. Moreover, growth rate after shear depends slightly on the deformation history while during shear it correlates with the molecular weight.

McHugh et al. [13] investigated the extensional flow of an UHWPE droplet in a four roll mill using point-wise birefringence and dichroism measurements on the outflow centerline. Flow birefringence showed an increase in orientation with distance from the stagnation point. After cessation of flow, birefringence showed complete relaxation of the carrier phase, while birefringence of the droplet phase showed retention of orientation and development of crystallinity. The maximum in birefringence intensity occurred on the outflow centerline and not in the stagnation point. The time to obtain this maximum increased for decreasing distance from the stagnation point. Initial crystallization was seen to be a function of both orientation and strain. It was suggested that the viscoelastic molecular strain due to flow orientation might be the controlling process for enhancing crystallization.

Blandell et al. [34] and Mahendrasingam et al. [35] performed in-situ WAXS experiments at the micro-focus beam-line of the ESRF on fast drawing of PET close to T_g. Three different regimes were observed. In the first regime, corresponding to low temperatures and high draw rates, orientation was insensitive to draw rate and was mainly in drawing direction. The onset of crystallization was delayed until the end of deformation. In the third regime, corresponding to high temperatures and low draw rates, no oriented structures were observed. In the second regime, corresponding to intermediate temperatures and draw rates, orientation decreased with increasing temperature and decreasing draw rate, and was tilted with respect to the drawing direction. The tilting in the orientation was explained by the interaction of the nuclei formed with the surrounding network. The onset of crystallization could be seen before the end of drawing. The difference in onset in the first two regimes was ascribed to the lack of freedom and mobility to organize chains into crystals during deformation at high deformation rates. The strain-induced crystallization rate was found to be insensitive to temperature, and was explained by two counteracting processes. An increase in temperature reduces the crystallization rate as a result of lower network orientation for a given deformation rate, this is counteracted by the influence of increased molecular mobility on crystallization kinetics.

One of the few studies on the influence of nucleation agents on flow-induced crystallization was by Jerschow and Janeschitz-Kriegl [27] using a slit flow. Nucleating agents strongly enhanced shear-induced crystallization. Thick, highly oriented layers far into the core were found even for low molecular weight materials.

In this study, a cross-slot flow cell is used to investigate stress-induced crystallization in a complex flow with a strong elongational component. The main advantages of this confined geometry is the high attainable strain. Schoonen [8] compared the cross-slot flow with the flow around a cylinder and the contraction flow, and concluded that the highest strain, combined with constant strain rate is obtained in a sufficiently large area in the cross-slot flow geometry. Even higher strains can be obtained in fiber spinning experiments, but here both thermal and deformation history are not well defined and, moreover, the basically unknown deformation history in extruder and die could be of influence. A second advantage of the cross-slot flow device is the wide range of materials that can be investigated. No specific material properties are necessary, like spinability. A third advantage of this flow geometry is the centered stagnation point, which is of practical use in the WAXS measurements (in shear flows part of the scattering is absorbed by the walls). A last advantage is the compactness of the cell, which results in controllable thermal gradients and thermal history.

3 Modeling Aspects

3.1 Constitutive Models for the Stress Tensor

In this study, three constitutive equations were used, one generalised Newtonian and two viscoelastic equations. The Carreau-Yasuda viscosity model was used to compute the three-dimensional velocity field in the cross-slot device:

$$\tau = 2\eta D; \quad \eta = \eta_0 \left(1 + \left(\frac{\gamma}{I_2 D}^\alpha\right)^{\frac{1}{\alpha}}\right)^{-\frac{1}{\alpha}},$$

(1)

with $\eta_0$ the zero shear-rate viscosity, $\lambda$ the relaxation time, $n$ the power law parameter and $I_2$ the second invariant of the deformation rate tensor $D$. The parameter $\alpha$ controls the transition between the zero shear-rate and the power law region.

To compute the viscoelastic stress distribution in a decoupled way, two non-linear models were used: theLeonov and the extended Pompom model. The Leonov model excellently captures the (non)-linear viscoelastic behavior in shear flows if multi modes are used; elongation is, however, less accurately described, see e.g. Larson [36]. The differential form of the Leonov model is given by (for one mode)

$$\tau + \frac{1}{\lambda} \tau + \frac{1}{2G \lambda} \left(\frac{\gamma}{I_2 D}^\alpha\right)^{1+\alpha} = 2GD,$$

(2)

The parameters can be determined by fitting linear viscoelastic data only. For incompressible, planar deformations, part (a) of Eq. 2 is equal to zero (and the Giesekus model with $\alpha = 0.5$ remains).

The Pompom model, McLeish and Larson [37], separates stretch and orientation of a polymer molecule. The original approximative differential model showed discontinuities in steady state elongation and no second normal stress difference, which was shown to influence flow-induced crystallization, Jerschow and Janeschitz-Kriegl [26]. Verbeeten et al. [38] proposed an extended version of the Pompom model (XPP), which improved upon these two disadvantages. Excellent quantitative agreement with measurements of branched (LDPE) and linear polymers (HDPE) was found by using a multi mode version.

The differential equation of the XPP model is given by (for one mode)

$$\tau + \frac{1}{\lambda(\tau)} \tau = 2GD,$$

(3)
with the relaxation tensor
\[
\frac{1}{\lambda(\tau)} = \frac{1}{\lambda_{ob}} \left[ \frac{\alpha}{G} \tau + \frac{1}{f(\tau)} I + G \left( \frac{1}{f(\tau)} - 1 \right) \tau^{-1} \right]
\] (4)
and the extra function
\[
\frac{1}{\lambda_{ob} f(\tau)} = \frac{2}{\lambda_{oo}} \left( 1 - \frac{1}{\Lambda} \right) + \frac{1}{\lambda_{ob} \Lambda} \left( 1 - \frac{\alpha J_2}{3 G^2} \right).
\] (5)

Backbone stretch and stretch relaxation time are defined as
\[
\Lambda = \sqrt{1 + \frac{J_2}{3 G^2}}, \quad \lambda_o = \lambda_{ob} \exp(-\nu(A - 1)), \quad \nu = \frac{2}{q},
\] (6)
in which \( q \) is the number of branches. Parameter \( \alpha (\alpha \geq 0) \) describes a Giesekus type of anisotropy, Bird et al. [39]. This parameter influences the second normal stress difference only. The Extended Pompom model is equivalent to the original approximative Pompom model for \( \alpha = 0 \). The orientation relaxation times of the backbone \( \lambda_{ob} \) are obtained from linear viscoelastic data. The number of branches \( q \), the stretch relaxation times \( \lambda_o \) and the anisotropy parameter \( \alpha \) are determined for each mode. For both models the corresponding recoverable strain tensor \( B_e \) is given by
\[
B_e = \left( \frac{\tau}{G} \right) + I.
\] (7)
The second invariant of the deviatoric part of \( B_e \) is used in the next section as the driving force for flow-induced nucleation and crystallization.

### 3.2 Constitutive Equations for Quiescent and Flow-induced Nucleation and Crystallization

Two sets of equations were used to model quiescent and flow-induced crystallization, respectively. Non-isothermal crystallization of spherulites was described by the Schneider’s rate equations [40], a set of differential equations for the structure, developing in quiescent conditions. Mean number of spherulites and their mean radius, surface and volume were calculated, Eqs. 8 to 11:
\[
\begin{align*}
\psi_3 &= 8 \pi \alpha, \quad (\psi_3 = 8 \pi N) \quad \text{rate}, \\
\psi_2 &= G \psi_3, \quad (\psi_2 = 8 \pi R_{tot}) \quad \text{radius}, \\
\psi_1 &= G \psi_2, \quad (\psi_1 = S_{tot}) \quad \text{surface}, \\
\psi_0 &= G \psi_1, \quad (\psi_0 = V_{tot}) \quad \text{volume}, \\
\psi_0 &= -\ln(1 - \xi_g) \space \text{space filling},
\end{align*}
\] (8 to 11)
with \( \alpha \) the nucleation rate and \( G \) the growth rate. Impingement of spherulites is captured by an Avrami model, Eq. 12. The morphology is described per unit volume by the total volume of spherulites \( V_{tot} \), their total surface \( S_{tot} \), the sum of their radii \( R_{tot} \) and the number of nuclei \( N \). The relation of these parameters with \( \psi_i \) is given between brackets. The number of nuclei and the growth rate have to be measured as a function of temperature. Relations for these properties will be given in section 4.

For flow-induced crystallization, the model of Eder and Janeschitz-Kriegl [2] was used. Zuidema [41, 42] proposed a modification of this model and used the recoverable strain, computed with the Leonov model, rather than the shear rate as a driving force, the \( S_2 \)-model. He showed that flow-induced structures correlate most strongly with the viscoelastic mode with the highest relaxation time. Therefore, only the second invariant of the deviatoric part of the recoverable strain \( J_2(\mathbf{B}_e^2) \) for the largest rheological relaxation time was used. This invariant can be considered as a measure for the molecular orientation, Larson [36].

The \( S_2 \)-model has the same structure as Schneider’s rate equations. Mean number of shish-kebabs and their mean length, surface and volume are calculated, Eqs. 13 to 16:
\[
\begin{align*}
\psi_3 &= \frac{\psi_3}{\tau_n} = 8 \pi J_2 g_n', \quad (\psi_3 = 8 \pi N) \quad \text{rate}, \\
\psi_2 &= \frac{\psi_2}{\tau_1} = \psi_3 J_2 g_n'/g_n, \quad (\psi_2 = 4 \pi L_{tot}) \quad \text{length}, \\
\psi_1 &= G \psi_2, \quad (\psi_1 = S_{tot}) \quad \text{surface}, \\
\psi_0 &= G \psi_1, \quad (\psi_0 = V_{tot}) \quad \text{volume}, \\
\psi_0 &= -\ln(1 - \xi_g) \space \text{space filling},
\end{align*}
\] (13 to 16)
with \( J_2 \) the driving force, \( G \) the growth rate, \( g_n' \) and \( g_n \) scaling factors to describe the sensitivity of flow-induced nuclei and length on \( J_2 \), and \( \tau_n \) and \( \tau_1 \) characteristic times to describe the relaxation behavior of flow-induced nuclei and length, respectively. Impingement of the cylindrical structures formed is again captured by an Avrami model, Eq. 17. 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 \( N \). The relation of these parameters with \( \psi_i \) is given between brackets.

Their meaning is as follows: flow-induced molecular orientation can generate extra nuclei, Eq. 13. When the orientation is strong enough, these nuclei grow out in one direction, Eq. 14. The radial growth rate of the cylindrical structures is taken equal to the spherulitical growth rate, see Eq. 15. According to Tribout et al. [23] growth rate depends weakly on flow after cessation of flow. Of course, other choices for the radial growth dependent on \( J_2 \) are possible. The relaxation time \( \tau_1 \) is in general taken very large, because reduction of length can only occur via melting. The relaxation time \( \tau_n \) was chosen equal to the rheological relaxation time.

Zuidema [41, 42] considered nucleation as physical cross-linking. Consequently, an increased number of nuclei causes an increase in the rheological relaxation time. The most simple form of a linear relationship between flow-induced nuclei and the highest rheological relaxation time was chosen.
\[
\theta_i = a_T(T) \theta_0 \left( 1 + \frac{BN \xi_g}{g_n'} \right),
\] (18)
with \( \theta_0 \) the highest rheological relaxation time at the reference temperature, \( a_T \) the shift factor and \( B \) a scaling factor that describes the interaction between nuclei and rheology. Consequently, the scaling factors \( B, g_n' \) and \( g_n \) should be measured as a function of flow conditions.
with \( c_1 \) and \( c_2 \) the WLF constants. The Maxwell parameters (\( G_i, \lambda_i \)) were determined by fitting the Maxwell model on the linear viscoelastic data. The dynamic moduli are given by

\[
G' = \sum_{i=1}^{N} G_i \lambda_i^2 \omega^2, \quad (21)
\]

\[
G'' = \sum_{i=1}^{N} G_i \lambda_i^2 \omega^2, \quad (22)
\]

with \( N \) the number of modes. The number of nuclei is described by

\[
N(T) = N_{ref} \exp\left\{-c_N(T - T_{ref})\right\}, \quad (23)
\]

with \( N_{ref} \) the number of nuclei at the crystallization reference-temperature \( T_{ref} \) and \( c_N \) a constant. The growth rate data could be described by a linear exponential function between 120 and 150 °C, see Swartjes [43]:

\[
G(T) = G_{ref} \exp\left\{-c_g(T - T_{ref})\right\}, \quad (24)
\]

with \( G_{ref} \) the growth rate at the crystallization reference temperature \( T_{ref} \) and \( c_g \) a constant.

The \( S_{12} \) parameters for StamylanP 13E10 could not be determined. Therefore also simulations were performed with the well-characterized Daplen KS10 (iPP with molecular weight of 235 kg/mol and molecular weight distribution 3.1, Borealis) to show the quantitative behavior of the \( S_{12} \) model in the cross-slot flow cell. The characterization was performed by the Linz group, Eder and Janeschitz-Kriegl [2], and summarized in Table 3. The \( S_{12} \) parameters were determined by Zuidema et al. [41], and are also shown in Table 3. The XPP parameters could not be determined, because for this polymer no uniaxial elongation data were available. The growth rate data of Daplen

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</thead>
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<tr>
<td>0.210 K(^{-1} )</td>
<td>140 °C</td>
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Table 3. Parameters of Daplen KS10 and fits for the WLF equation, the Maxwell and the Carreau-Yasuda model (\( T_{ref} = 200 °C \)), the number of nuclei and growth rate, and the parameters for the \( S_{12} \) model. Notice that a quadratic exponential function was used to describe the growth rate (Eq. 25). Original data were from Eder and Janeschitz-Kriegl [2] and Jerechow [64]. The \( S_{12} \) parameters were determined by Zuidema [41].

In case of flow, both spherulitical and flow-induced structures contribute to the degree of space filling, depending on the influence of \( J_2 \). The Avrami model for impingement is then described by

\[
\psi_0 + \psi_0 = -\ln(1 - \xi_g). \quad (19)
\]

### 4 Materials and Methods

#### 4.1 Materials

Experiments were carried out on StamylanP 13E10, an isotactic polypropylene provided by DSM, with molecular weight of 501 kg/mol and molecular weight distribution 6.0. Rheological characterization was performed in simple shear and uniaxial elongation. The determination of the number of nuclei and the growth rate were performed using a hotstage under a microscope see Swartjes [43]. The parameters resulting from this characterization are summarized in Table 2. The WLF equation is defined by

\[
\log(a_T) = -\frac{c_1(T - T_{ref})}{c_2 + (T - T_{ref})}, \quad (20)
\]

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KS10 were described by a quadratic exponential function, Eder and Janeschitz-Kriegl [2].

$$G(T) = G_{\text{ref}} \exp \left\{ -cG(T - T_{\text{ref}})^2 \right\}. \quad (25)$$

These two examples clearly demonstrate one of the problems in modelling of flow-induced nucleation and crystallization. One really need well-characterized materials, which requires a multitude of different experiments and skills. Completely characterized materials do not exist, yet.

### 4.2 Experimental Methods

#### 4.2.1 Cross-Slot Flow Cell

A schematic of the cross-slot flow cell together with its dimensions are given in Figs. 1 and 2. The cell consists of two curved reservoirs and a cross-slot. The dimensions of the inflow and outflow channels are 45 x 2 x 2 mm$^3$ (length x height x depth), and of the reservoirs are 5 x 2 mm$^2$ (height x depth). The cell is fully insulated and fixed to a frame. Insulation is required to reduce heat losses and thermal gradients. Flow is created by rotating a ring with two cams over 90 degrees by a DC-motor (Maxon motor, planetary gearing with a ratio of 236:1) connected with two steel cables to the ring. The movement of the ring was measured with a linear displacement transducer (Lucas Schaevitz). The frame was mounted on a vertical (Newport; M-MTM200PP.1) and a horizontal translation stage (Newport; UZM160PP.05), respectively, to control the position of the cell. To compensate for shrinkage and possible leakage, two extra reservoirs were added and connected with the original reservoirs. In this extra reservoir, a sample volume of $\approx 8.2 \times 10$ mm$^3$ was pressurized using a metal spring (not shown in Fig. 2A).

The depth-to-height ratio is chosen equal to 1.0. For ease of interpretation of the flow, depth-to-height ratios larger than eight are preferred to obtain a two dimensional flow. However, the depth-to-height ratio is limited by the maximum scattering angle in WAXS, and three-dimensional effects have to be accepted. For optimum transmittance the depth of the channels was chosen equal to 2 mm. X-ray scattering is not influenced by the metal corners in a circular region of about 1 mm in diameter around the center.

Three oil baths (LAUDA K 6 KP and UB 20) were used to impose a desired thermal history. One to define the annealing and flow temperature, the second (at a low temperature, 30°C) for cooling and the third (the largest LAUDA UB 20) for the crystallization temperature. Three mechanical valves (Klinger), designed such that only one oil bath is connected with the flow cell, are remote controlled with pneumatic rotators (Bar GmbH).

The flow cell is heated by two spiral oil channels in the two plates next to the sample. Temperature was measured close to the center and close to the upper reservoir of the cell. Diamond windows (Drukker International, Cuijk, The Netherlands) are used for the X-ray experiments because the absorption coefficient of this material in the wavelength range 0.7 to 1.0 Å is low. An extra advantage of diamond is its large thermal conductivity, giving almost no thermal gradients in the sample. As a disadvantage, the birefringence in diamond windows is quite high. Therefore, Schott SF57 glass is used as window material for the birefringence experiments, despite its lower fracture strength (and therefore larger window thicknesses needed) and low thermal conductivity yielding larger thermal gradients in the sample. Resulting temperature gradients in the polymer prove to be negligible in case of diamond, but they are relatively large (in the order of 0.5°C in the depth of the cell) in case of SF57 (see Swartjes [43, Appendix D]).

The diamond windows have a thickness of 0.25 mm, a diameter of 4.2 mm, and are glued in a stainless steel frame (clear aperture 3.2 mm) (Fig. 2B). The diamond windows were polished to an optical surface quality, having the following specifications: parallelism of main sides $\leq 5$ arcmin, flatness $\leq 650$ nm/mm$^2$ and roughness (P-V value) $\leq 20$ nm. The low roughness value was chosen to reduce possible nucleation on the window. However, it is unknown which value is sufficient.
to neglect this influence. The low-birefringent SF57 glass windows have a thickness of 1.8 mm, a diameter of 6 mm, and are also glued to a stainless steel frame (clear aperture 5.0 mm).

4.2.2 Set-up for Birefringence Experiments

The optical train for field-wise birefringence experiments is shown in Fig. 3. The train is fixed, while the flow cell is mounted on a traverse system. A HeNe-laser with a wave length of 632.8 nm is used in combination with a beam expander to obtain a parallel light beam with a diameter of about 15 mm. The first polarizer is used to set the intensity hitting the camera. The polarization state generator consists of a polarizer and a quarter wave plate, which is placed at an orientation angle of 45 degrees relative to the second polarizer. The polarization state analyzer also consists of a polarizer and a quarter wave plate, which are placed at an orientation angle of 135 and 90 degrees, respectively, relative to the second polarizer. Orientation of the polymer chains is expected to be in outflow direction. Therefore, the optical train is mounted at 45 degrees with respect to the outflow channel of the flow cell, to obtain the maximum intensity on the outflow centerline, see Fuller [44, Section 8.2.2.]. Birefringence is visualized with a camera (Panasonic WV-CD130) in combination with a microscope (Zeiss SV-11).

![Fig. 3. Optical train for field-wise birefringence measurements](image)

4.2.3 Set-up for WAXS Experiments

The Wide Angle X-ray Scattering experiments were carried out in Grenoble (France) at the materials beam-line ID13 of the European Synchrotron Radiation Facility (ESRF), where a high X-ray flux allows for time-resolved experiments. The combination of a high flux and a micro-focus beam in order to measure in-situ structure development locally, is fulfilled at the micro-focus beam-line. A beam-size of 0.2×0.2 mm² was used at the materials beam-line (ID11). The collimator-to-sample distance and the beam-stop-to-sample distance were about 80 mm and 100 mm, respectively. The detector was a Frelon CCD detector having a measuring area of 179×179 mm² (1024×1024 pixels with a horizontal and vertical pixel size of 175 μm) and a dynamic range of 14 bit. The exposure time was 5 s, the sample-to-detector distance was 377 mm, and the wavelength used was 0.718 Å. All images were corrected for spatial distortion using the ‘Fit2d’ software of the ESRF, Hammersley et al. [45].

4.3 Numerical Method

Since three-dimensional finite or spectral element calculations with non-linear viscoelastic models are expensive and time consuming, the calculation of the velocities and stresses were performed in a decoupled way, Douven et al. [46]. The 3D, generalised Newtonian velocity field was computed with the finite and spectral element package SEPRAN, Segal [47], using the Carreau-Yasuda model. Only the inner part of the cross was modeled to minimize computational costs and use all computational capacity to obtain a high accuracy for the velocity. Moreover, due to symmetry, only one eight of the cell was modeled. The spectral element mesh consisted of 32, eight order elements giving 18.785 nodal points. The inflow and outflow length are equal to 2.5 mm and the height and width of the mesh are both equal to 1.0 mm.

Next, the deformation history for some user defined points was determined by tracking particles using the velocity field. Velocities and velocity gradients were determined on these paths by using the polynomial basis functions, Anderson [48]. Finally, stresses and stress related properties were calculated using the two viscoelastic constitutive equations mentioned: Leonov and XPP. All modes of the time relaxation spectrum were used to determine the stresses, while only the highest relaxation time is used for the calculation of the orientation parameter (the second invariant of the deviatoric part of the elastic Finger tensor). A first order implicit Euler scheme is used to determine the stress, the quiescent part and the flow-induced part of the crystallization.

The influence of an undershoot in temperature was taken into account by keeping all nuclei that were created at the lowest temperature, while the growth rate was dependent on the instantaneous temperature.

5 Experimental Results

5.1 Birefringence Experiments

Field-wise birefringence experiments were performed using StamylanP 13E10 to check the experimental conditions and to find an useful experimental time range. Only qualitative results are presented. Flow was created at the crystallization temperature to show flow-induced enhancement of crystallization at rather extreme conditions.

The sample was annealed at 215 °C for one hour, and cooled, $T \approx 25\, ^\circ\text{C}$/min to the flow or crystallization temperature. Next, flow was created after about 30 min. The elongational rate, e-
Estimated by dividing the mean velocity in the inflow channel by half the channel height, was about 0.4 s⁻¹. Flow times of 440 s and 780 s were applied at 145 and 155 °C, respectively.

Both experiments showed one large, broad, flow-induced fringe at both ends of the inflow channel, and high orientation on the outflow centerline during flow. At 145 °C a fiber-like structure was found on the outflow centerline, Fig. 4A. Close to this structure other small fringes were found (see insert Fig. 4A). After flow the high intensity on the centerline remained at 145 °C, while it relaxed slowly at 155 °C.

Typically, the streamlines of the preceding flow could be observed in the experiment at the lower temperature, Fig. 4C. This structure is probably (flow-induced) crystallization on and close to the optical windows. The small fringes close to the outflow centerline observed during flow, were also observed after flow (during the first 20 min).

The relaxation on the inflow centerline at 155 °C (the black line in Fig. 5A) is shown in Fig. 5B. The stagnation point does not remain exactly in the same position. The y-position of the stagnation point changes from slightly positive during flow, to a small negative value during relaxation.

The stationary stress levels in the cross-slot flow can be accurately de-

\[ \text{Fig. 4. Field-wise birefringence measurement on StamylanP 13E10 in the cross-slot flow cell} \]
\[ \text{A: during flow, three minutes after starting the flow (145 °C and } v \approx 0.4 \text{ s}^{-1}. \text{ Outflow or } x \text{-direction is vertical and inflow or } y \text{-direction is horizontal. Insert: a close-up of the region around the stagnation point} \]
\[ \text{B: 4 min, C: 10 min, D: 20 min after cessation} \]

\[ \text{Fig. 5. Relaxation behavior of StamylanP 13E10 in the cross-slot flow cell at 155 °C} \]
\[ \text{A: 20 s after cessation of the flow. Contrast was enhanced using histogram equalization in Matlab (The Mathworks, Inc.); B: contour plot of the relaxation of the birefringence on the inflow centerline (black line in Fig. 5A). The cessation of flow starts at } t = 0 \text{ s} \]
scribed by the Pompon model, Verbeeten et al. [49]. However, optical properties are strongly varying along the propagation direction of the light beam in this three-dimensional flow. A quantitative comparison can only be obtained using the differential propagation matrix theorem, Azzam [50], see also Fuller [44] or Schoonen [8]. Moreover, the point-wise polarization modulation technique of Fuller and Mikkelsen [51] is recommended to obtain a continuous and more sensitive birefringence value.

5.2 WAXS Experiments

Measurements at the micro-focus beamline ID13 of the ESRF were performed to investigate the structure on the inflow and outflow centerline close to the stagnation point. About the same experimental conditions were applied as for the birefringence experiment shown in Fig. 4. The sample was annealed at a temperature of 220 °C for 90 min. Next, it was cooled (with 32.7 °C/min) to a flow and crystallization temperature of 148.4 °C. Flow was applied at this temperature to enhance the deformation effects, since relaxation of stresses will be limited. Finally, a low flow rate (≈ 0.4 s⁻¹) was applied for 820 s after waiting about 30 min, and crystallization was monitored. During flow no crystalline structures were found in nine points around the stagnation point (x = –0.8 : 0.8 : 0.8 mm and y = –0.8 : 0.8 : 0.8 mm). Crystalline peaks were observed from about 200 s after cessation of flow. The reflections were weak on the inflow centerline and only (040) was oriented parallel to the outflow direction, Fig. 6A. Close to the stagnation point, in the stagnation point and at the outflow centerline, both (110), (040) and (130) were oriented in the outflow direction, Fig. 6B. Notice that the stagnation point is not found at point (0,0). This was also observed in the birefringence experiments.

The integrated WAXS intensities for the inflow and outflow centerline are shown in Fig. 7. On the inflow centerline, the peak intensities become larger close to the stagnation point. On the outflow centerline, it seems that the intensities are slightly more pronounced further from the stagnation point. The size of this oriented structure, with orientation in (110), is 80 μm in inflow, Fig. 8A, and at least 2 mm in outflow direction, Fig. 8B. Orientation in (040) was found in all points, Fig. 9.

The effect of flow at high temperature on crystallization at low temperature was next investigated (analogous to the shear experiments in Vleeshouwers and Meijer [29]). Measurements on five positions on the outflow centerline were performed at beam-line ID11 of the ESRF. A quiescent and a flow experiment were performed. After annealing at 220 °C for 60 min, the sample was cooled (with 15.6 °C/min) to a crystallization temperature of 134.1 °C. In case of the flow experiment, flow was created at 220 °C for 44 s with an elongational rate in the stagnation point of about 7.0 s⁻¹, after which the sample was cooled to Tc. The undershoot in tempera-
ture was equal to 3.2 and 2.5 °C, for the quiescent and flow experiment, respectively.

The two dimensional WAXS patterns were integrated along the Debye ring. Next, the peak area was integrated to obtain a measure for the crystallinity, and plotted as a function of time for five points on the outflow centerline in Fig. 10. Crystallization rates are higher if flow was applied, however, the X-ray patterns didn’t show any indication of orientation. This could be due to the ‘large’ beam size (0.2×0.2 mm²) used. These conclusions did not change when flow was applied at 170 °C and the influence of flow was much less pronounced than anticipated. Numerical simulations were used to explain these findings, focusing on the influence of shear gradients in the depth of the flow cell.

6 Numerical Results

In the simulations the characteristics of Daplen KS10 are used, because its crystallization behavior is known both in quiescent conditions and after flow, see Table 3. The recoverable strain modeled with the Leonov model is used as the driving force.

A flow rate of $1.85 \times 10^{-8}$ m³/s is applied (in one inflow channel) for 40 s at a temperature of 200 °C. Next, the sample is cooled with a cooling rate of 30 °C/min to an isothermal crystallization temperature of 140 °C. Time $t = 0$ s is defined as the time reaching $T_c$. Space filling during crystallization is calculated in ten planes in depth ($z = 0.05 : 0.1 : 0.95$ mm) for 150 points. Some extra points are used close to the outflow centerline.

The predicted space fillings in the planes $z = 0.05$ mm and $z = 0.95$ mm are shown in Fig. 11. Large values are found close to the outflow stagnation line and in the corner (Fig. 11A). The influence of the shear rate components $\gamma_{xy}$ and $\gamma_{yz}$, which are more pronounced close to the windows, are shown in Fig. 11B. The average space filling is raised to a value of about 0.40. Interestingly is the increasing value close to the outflow centerline with increasing x-coordinate. The low value for the space filling at the corner is caused by the low shear rates in this region.

The averaged space filling (mean value of the space fillings in the ten planes) is shown in Fig. 12A. The behavior looks similar to Fig. 11 and, although the influence of shear flow is less pronounced, the increase at the outflow centerline is still observed.

The dependence of space filling on the depth of the cell is calculated in four characteristic points, Fig. 12B. Close to the stagnation point space filling decreases with depth and increases slightly close to the wall. In the point close to the corner space filling decreases continuously with depth, while in the point on the outflow centerline it increases with depth. This point shows most clearly the influence of the shear rate in the neutral direction, because its value is zero in absence of shear rate (in the plane $z = 0$ mm). The largest changes are found in the point on the outflow centerline. Initially, its value is very close to the value in the stagnation point and decreases with depth, but it increases rapidly close to the wall. In conclusion, three-dimensional effects are considerable for the depth-to-height ratio of the flow channels that had to be compromised, see section 4.
For future optimization of the experiments, the influence of the flow time, rate, temperature, the depth-to-height ratio and the rounding of corner are investigated. An infinite residence time is only obtained for a particle positioned in the stagnation point, however this particle has no dimensions. The residence time in realistic points is finite and depends on the position and the flow rate, and is typically in the order of a few seconds for the flow rate of \(1.85 \times 10^{-8} \text{ m}^3/\text{s}\) applied. For example, it is about 0.7 s in the plane \(z = 0.05 \text{ mm}\) and 7.4 s in the plane \(z = 0.95 \text{ mm}\) for a point close to the stagnation point \((1 \times 10^{-6}, 5 \times 10^{-3})\).

As a consequence, to obtain the maximum orientation around the stagnation point, it is not necessary to use the full stroke (90 degrees rotation) of the ring, which corresponds to an experimental time of 40 s. A shorter flow time would give the same results for points close to the outflow stagnation line and will result in less influence of shear rates, Fig. 13 (compare with Fig. 11).

Lowering the flow rate, lowers the total influence of \(B_e\) (elastic part Finger tensor) for particles that suffered shear gradients, but for particles close to the outflow stagnation line it remains about the same, since they travel with a lower velocity, but also for a longer time, see Schoonen [8]. Lowering the flow with a factor 10 decreases space filling, see Fig. 14. Although indeed the influence of the shear rates is now relatively smaller with respect to the maximum found close to the outflow stagnation line, the total space filling has been reduced with a factor 25.

Decreasing the flow temperature and applying the same flow rate will cause apparent larger shear rates. Therefore, the flow will be more plug-like and three-dimensional effects will be smaller. Increasing the depth-to-height ratio of the channels within the cell of course reduces three-dimensional effects. A calculation was performed for a depth-to-height ratio of two, using the same amount of spectral elements as in the other calculations, see Fig. 15. The influence of \(\gamma_{12}\), close to the corner in plane \(z = 0.05 \text{ mm}\) is not changed, but the influence of \(\gamma_{13}\) in the plane \(z = 0.95 \times D\) mm is lowered from 0.40 to 0.16.

Finally, rounding the corners was found to decrease the actual channel depth-to-height ratio and therefore, increase three-dimensional effects. For a radius \(R < 0.5 \times H\) (\(H = \text{channel height}\) three-dimensional effects prove to be small, while for \(R > 0.5 \times H\) they were more pronounced, see Swartjes [52].

<table>
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<tr>
<th>(Q, \text{m}^3/\text{s})</th>
<th>(t_f, \text{s})</th>
<th>(D/H)</th>
<th>(\xi_{12} %, \text{n}_g)</th>
<th>(\xi_{13} %, \text{n}_g)</th>
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</thead>
<tbody>
<tr>
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<td>5</td>
<td>1</td>
<td>1.8</td>
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<tr>
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<td>1</td>
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<tr>
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<td>40</td>
<td>2</td>
<td>17.5</td>
<td>12.8</td>
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</table>

Table 4. Influence of the variation of the flow rate \(Q\), flow time \(t_f\) and the depth-to-height ratio on the relative space filling. \(\xi_{12}\) gives the influence of \(\gamma_{12}\) and is defined as \(\xi_{12}(0.9, 0.95, 0.05 \times D)/\xi_{12}(1 \times 10^{-6}, 5 \times 10^{-5}, 0.05 \times D)\), \(\xi_{13}\) gives the influence of \(\gamma_{13}\) and is defined as \(\xi_{13}(1 \times 10^{-6}, 0.95, 0.95 \times D)/\xi_{13}(1 \times 10^{-6}, 5 \times 10^{-5}, 0.05 \times D)\).
The results of all calculations shown in Fig. 13 to 15 are summarized in Table 4. The influence of the shear rate \( \gamma_{12} \) is seen in the point close to the corner in the plane \( 0.05 \times D \), while the influence of \( \gamma_{13} \) can be seen on the inflow centerline in the plane \( 0.95 \times D \). Therefore, the values of the space filling close to the corner in plane \( 0.05 \times D (g_{12}) \) and on the inflow centerline in plane \( 0.95 \times D (g_{13}) \) are given, and normalized with the space filling value close to the stagnation point (1-10^-6, 5-10^-5) in plane \( 0.05 \times D \). A lower value of the flow rate or a larger depth-to-height ratio reduces the influence of \( \gamma_{13} \) with respect to \( \gamma_{12} \). By far, the largest influence is seen in reducing the flow time.

7 Discussion

Structure development in the cross-slot flow device was analyzed, experimentally and numerically. A qualitative agreement was found between the two experimental methods used (flow at low and at a high temperature prior to isothermal crystallization) and the numerical prediction.

An highly oriented structure was found in the birefringence en WAXS experiments. The birefringence experiments showed that this structure survived up to 20 min after cessation of flow, when flow was applied at the crystallization temperature. The presence of the front and back wall (the optical windows) caused the occurrence of ‘streamlines’. This phenomenon can be explained by the influence of shear gradients close to the windows. Moreover, crystallization at the windows is enhanced due to the thermal gradient in the depth of the cell introduced by the optical windows (Schott SF57 glass).

The WAXS experiments showed an highly oriented structure close to the outflow stagnation line, having orientation in the (110), (040) and (130) reflections. An increase of orientation in (110) and (130) corresponds to an increasing material ordering. Nadella et al. [53] observed higher orientations for larger molecular weights. An off-equator arcing in (110) and (130) corresponds to the daughter lamellae, which grow in the a* direction (or flow direction, see Fig. 17). A rotation around the b-axis will only affect the non-(0k0) planes (in this case (110) and (130)). This explains the orientation in (040) in Fig. 16B, C), while the structure is branched. In highly oriented samples (Fig. 16D, a fiber-like structure is seen with equatorial reflections in (110), (040) and (130). Fujiyama proposed a structure as given in Fig. 17 corresponding to the WAXS pattern in Fig. 16C. It is a branched shish-kebab structure. The orientation in both (110) and (130) in our experiments corresponds to a highly oriented, non-branched structure. WAXS experiments showed that large flow rates also create a large influence of the shear gradients in the height and depth of the flow channel. The effects of flow on crystallization close to the outflow centerline was not as pronounced as expected.

The influence of the shear gradients can be reduced by using a shorter flow time and/or using a cell with a larger depth-to-height ratio. However, the experimental set-up should be able to allow for experiments with large elongational rates also at temperatures below the melting temperature, to investigate the influence of relaxation. This is not possible with the current set-up, because of the mechanical

Fig. 15. As Fig. 11 with a twice larger D/H ratio
A: plane z = 0.05 × D mm, B: plane z = 0.95 × D mm

Fig. 16. Two-dimensional WAXS patterns of α-iPP. Flow direction was vertical. Sample orientation increases from A to D.
A: core of an injection moulded sample, Fujiyama and Wakino [65], Kalay et al. [66]
B: oriented part of α-spherulite, Norton and Keller [67], and unidirectional crystallized sample, Lovinger [68]
C: skin of an injection moulded sample, Fujiyama and Wakino [65], SCORIM (Shear Controlled Orientation Injection Moulding) sample, Kalay et al. [66], during melt spinning, Nadella et al. [53], stretching above the melting temperature, Andersen and Carr [69], and a short time shear experiment at 141 °C, Kumaraswamy et al. [30]
D: stretched near the melting temperature, Andersen and Carr [69]

Fig. 17. Proposed lamellar branched shish-kebab structure in the skin of an injection moulded sample, Fujiyama and Wakino [65]. Flow direction is vertical

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The advantage of the SJ2 model above the Eder rate equations is the time. This means that the scaling factor gives an increase in the number of branches and relaxation model in rather natural way. Increase in the number of nuclei nucleation in the Leonov model can be used in the Pompom model in rather natural way. Increase in the number of nuclei and rheological relaxation time has to be determined from experiments.

The mutual dependence of rheology and nucleation is modeled by physical cross-links, resulting in an increased relaxation time. The sensitivity of this relation between number of nuclei and rheological relaxation time has to be determined from experiments.

The concept of the equivalence of physical cross-linking and nucleation in the Leonov model can be used in the Pompom model in rather natural way. Increase in the number of nuclei gives an increase in the number of branches and relaxation time. This means that the scaling factor \( \beta \) in Eq. 18 is related to the number of branches in the Pompom model.

Originally, the extended Pompom model was proposed for branched polymers, but it captures also the physics for linear polymers, as shown by Verbeeten et al. [38] for HDPE. There are two big advantages when applying this model for the linear polymers used in this study. First, both elongation and shear data can be described excellent with the same set of parameters. Second, the physical description that serves as a basis for this model (i.e. the Pompom molecule) results in a more transparent model. The physical cross-linking process, proposed by Zuideema in the SJ2 model, can be related to the increase in the number of branches during crystallization.

Interesting is the intrinsic behavior of the two models used: Leonov and Pompom. This behavior was studied for StamylanP 13E10 without using the crystallization coupling (\( \beta = 0 \)). A flow rate of \( 1.85 \cdot 10^{-8} \text{ m}^3/\text{s} \) (in one inflow channel) for 40 s was used at a temperature of 200 °C. The strain hardening behavior in elongation for the Leonov model over-estimates the first component of the Finger tensor, Fig. 18, and therefore, the number of flow-induced nuclei, Fig. 19 for the SJ2 model. It is questionable whether these nuclei really exist at this temperature, but Fig. 19 is only presented to show the characteristics of the models.

### 8 Conclusion

A cross-slot flow cell was used to investigate stress-induced crystallization in a complex flow with a strong elongational component. The main advantage of this geometry is the high attainable strain at the free stagnation point. Three dimensional effects and temperature gradients in the flow cell increase the complexity of these measurements. Moreover, a large amount of material characterization experiments is essential to relate the thermo-mechanical history and crystallization in a quantitative manner.

An highly oriented structure was found in the cross-slot flow cell. This fiber-like structure without branches survived up to 20 min after the cessation of flow. The influence of flow applied at a temperature above the melting temperature is not as pronounced as expected. Numerical simulations showed that this is caused by the large shear gradients in the height and depth of the cell. The influence of both shear gradients are reduced if smaller flow times are applied, but still with the same residence time for particles close to the outflow centerline. Moreover, the shear gradient in the depth can be reduced if larger channel depth-to-height ratios are used.

The recoverable strain is the driving force in the flow induced crystallization model. Since the XPP model has proved superior in quantitative predictive power, it is strongly recommended to use this model to calculate the recoverable strain.