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Self-Regulation in Flow-Induced Structure Formation of Polypropylene

Peter C. Roozemond, Martin van Drongelen, Zhe Ma, Anne B. Spoelstra, Daniel Hermida-Merino, Gerrit W. M. Peters*

Flow-induced structure formation is investigated with in situ wide-angle X-ray diffraction with high acquisition rate (30 Hz) using isotactic polypropylene in a piston-driven slit flow with high wall shear rates (up to \( \approx 900 \, \text{s}^{-1} \)). We focus on crystallization within the shear layers that form in the high shear rate regions near the walls. Remarkably, the kinetics of the crystallization process show no dependence on either flow rate or flow time; the crystallization progresses identically regardless. Stronger or longer flows only increase the thickness of the layers. A conceptual model is proposed to explain the phenomenon. Above a certain threshold, the number of shish-kebabs formed affects the rheology such that further structure formation is halted. The critical amount is reached already within 0.1 s under the current flow conditions. The change in rheology is hypothesized to be a consequence of the “hairy” nature of shish. Our results have large implications for process modelling, since they suggest that for injection molding type flows, crystallization kinetics can be considered independent of deformation history.

1. Introduction

Flow-induced crystallization in polymer processing determines to a great extent the final product properties.\(^{[1,2]}\)

Especially at relatively low temperatures, i.e., between the melting point of crystals as measured during heating, and the crystallization temperature measured upon cooling, flow increases the number of nucleation sites, causing fine structures in the product’s morphology. If the flow is strong enough, it can even create anisotropic crystalline structures, known as shish-kebabs. These structures, consisting of a fibrous backbone with lamellar overgrowth, were first recognized in notably stirred undercooled solutions,\(^{[3,4]}\) and later also in polymer melts.\(^{[5]}\) Extensive research has been directed to the precise morphology of shish-kebabs. It was found that the shishes consist of regions of extended chain crystals connected by fringe-like amorphous regions, with kebabs formed by folded chain lamellae growing radially outward.\(^{[4,6]}\) A number of studies were directed to the minimal flow conditions needed to create these structures, expressed either in terms of stress,\(^{[7]}\) mechanical work,\(^{[8–10]}\) or backbone stretch.\(^{[11,12]}\) Long chains, although their concentration in shish-kebabs is not higher compared to the
rest of the material,[13] were proven to play a catalytic role in the formation of shish-kebabs.[7,12,14] Chain stretch being a prerequisite, decreasing mobility with molecular weight promotes the formation of shishes. The mechanism behind the longitudinal growth of shish also got attention. Because “point-like” nuclei[15] have been observed to appear before the formation of oriented structures,[16] it has been hypothesized that chains that are convected past the existing precursor, “streamers,” are tethered onto the nucleus and hence propagate the shish in lengthwise direction,[14] or that “point-like” nuclei align and merge together, forming a shish.[17] The difficulty in studying the growth of shish-kebabs in situ is the enormous speed at which these structures propagate, in the order of micrometers per second.[14] Conventionally, the acquisition time of X-ray scattering images, the most likely candidate for studying these phenomena, is too high to resolve shish growth.

Recent technical improvements at the BM26 beamline at the European Synchrotron Radiation Facility have enabled wide-angle X-ray diffraction (WAXD) acquisition with 30 Hz. In this paper, we study the mechanism behind shish growth by subjecting a polymer melt to flow in a slit at high wall shear rates (up to ~900 s⁻¹), combined with this in situ X-ray diffraction technique. The flow was ceased at various times to allow characterization of structural development afterwards by taking “snapshots” at different development stages of shish. A detailed picture of the growth of shish-kebabs results.

### 2. Experimental Section

We conducted experiments on an iPP homopolymer (Borealis HD601CF, M₁ = 365 kg mol⁻¹, Mₙ = 68 kg mol⁻¹) also examined in other crystallization studies.[18,19] Flow is applied in a confined slit flow geometry within a modified multi-pass rheometer (MPR), by simultaneously moving the two pistons between which the material is confined in the same direction. This setup allows for simultaneous probing of rheology, via pressure transducers positioned near both pistons, and structure development, through windows in the slit-placed halfway between both pistons. Detailed and full description of similar, earlier experiments are provided elsewhere.[20] Samples were molten at 220 °C for 10 min to erase thermomechanical history. Hereafter, the samples were cooled to a temperature of 145 °C and subjected to flow at different piston speeds for different flow durations (see Table 1).

Morphological and structural development were evaluated during flow and during subsequent isothermal crystallization using WAXD (wavelength λ = 1.033 Å) at the beamline BM26B[21] of the ESRF (Grenoble, France). During and immediately after flow, 2D patterns were recorded at a frequency of 30 Hz for a total time of 2 s using a Pilatus 300K detector. Subsequent isothermal crystallization was monitored in a higher azimuthal range (>90°) using a Frelon detector with an acquisition time of 2.66 s per frame and a total duration of 22 min. Patterns for background correction were acquired for each detector at corresponding acquisition times using an empty load geometry. In addition, a dark current (no X-ray exposure) was subtracted for the Frelon-recorded patterns to correct for readout noise.

Crystallinity was calculated from the radially integrated patterns as the ratio between the scattered intensity by crystals and the total scatter intensity. For the data collected with the Pilatus, the area of the reflection is given by the area underneath the (isotropic) baseline- subtracted scattering pattern. Regarding the patterns acquired with the Frelon detector, azimuthal scans of the (110) reflection were fitted by Lorentzian peaks, which were integrated to obtain the area of the peaks. Proper geometrical corrections were applied.[22] Examples of procedures for both detectors are given in Figure 1.

### 3. Results

The pressure drop signal for all experiments is presented in Figure 2. Reproducibility is observed to be excellent. Steady state is reached after 0.08 s for 120 mm s⁻¹ piston speed and 0.1 s for 100 mm s⁻¹. For high piston speeds, the pressure drop starts to increase at some point due to structure formation in the high shear rate regions near the walls, effectively decreasing the thickness of the channel while the volumetric flow rate prescribed by the pistons remains the same. After stopping the flow, the pressure relaxes quite rapidly, indicating that the majority of crystal growth happens at near atmospheric pressure.

The apparent crystallinity (apparent, as it is an average crystallinity over the slit, because the beam traverses

<table>
<thead>
<tr>
<th>Piston speed [mm s⁻¹]</th>
<th>Flow duration [s]</th>
<th>( \dot{\gamma}_w ) [s⁻¹]</th>
<th>( \sigma_w ) [x10⁵ Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.25</td>
<td>370</td>
<td>1.21</td>
</tr>
<tr>
<td>80</td>
<td>0.25</td>
<td>500</td>
<td>1.35</td>
</tr>
<tr>
<td>100</td>
<td>0.11–0.20–0.23–0.25</td>
<td>635</td>
<td>1.47</td>
</tr>
<tr>
<td>120</td>
<td>0.11–0.17–0.20–0.23</td>
<td>769</td>
<td>1.57</td>
</tr>
<tr>
<td>140</td>
<td>0.20</td>
<td>904</td>
<td>1.66</td>
</tr>
</tbody>
</table>
across velocity gradient direction) is shown for all shear times in Figure 3a.\(^{23}\) Time \(t = 0\) is the start of flow. As expected, a longer flow time results in a higher amount of crystalline structure and hence in a higher apparent crystallinity. For all flow conditions, we observe the characteristic S-shaped curve indicative of crystallization until impingement, which seems to occur around 100 s (this is also the expected time for impingement with inter-shish distance of \(\approx 100–200\) nm (Figure 4 and ref. [24]) and crystal growth rate of \(\approx 4\) nm s\(^{-1}\)). As the radius of shish is much smaller than the radius of the kebabs (Figure 4), all crystallinity is attributed to kebab growth. We conclude that the first 100 s show the crystallization of the shear layer near the walls with dense highly oriented crystalline structures. After impingement, apparent crystallinity continues to increase at a lower slope. For all experiments, the increase in apparent crystallinity between 100 and 1200 s is 8%. This is ascribed to crystallization with a lower degree of orientation, which usually takes place in a fine-grained layer with isotropic structures.\(^{25}\) or perhaps less densely packed shish, known as sausages.\(^{14}\)

Because the shear layer has fully crystallized after 100 s, and crystallinity in the fine-grained layer is still negligible at this time, the space filling within the shear layer can be quantified by normalizing the apparent crystallinity with the value at \(t = 100\) s. Doing so, we obtain Figure 3b. Surprisingly, the data overlap perfectly for all flow conditions for \(t > 3\) s. Hence, although the thickness of the shear layer grows with shear time, the crystallization kinetics within the layer are unaffected by flow rate or time. Only at short times (\(t < 3\) s), there is an observable difference, caused by the fact that the shear layer is formed at earlier times for the faster piston speeds. Therefore, there is already an observable crystallinity signal at short times, whereas for the slower piston speeds it takes some time for the shear layer to be created, therefore at short times the crystallinity is negligible. At longer times, this time delay becomes negligible. Because crystallization kinetics are a direct result of the crystalline structure, this implies that the crystalline structure is also identical for all flow conditions.

To verify this observation, we performed TEM on a sample obtained at the strongest flow condition (140 mm s\(^{-1}\) for 0.2 s). The sample was prepared and analyzed in the same way as in ref. [19]. Figure 4 shows pictures obtained within the shear layer at two locations separated by 350 \(\mu m\) in velocity gradient direction. Indeed the morphology in both pictures looks very similar. This is also shown by the Fourier transforms of the TEM pictures (inserted). The positions of the lobes on the equator relate to long spacing of the kebabs and the streaks on the meridian indicate the distance between shish. These show no observable difference between the two positions where TEM pictures were taken. Hence these results confirm that crystalline morphology within the shear layer does not depend on position.

It can be hypothesized that structure formation influences the rheology of the material, increasing resistance to deformation, which at a certain point stops further growth of shish and therefore results in a saturation of shish density. The capability of our set-up to simultaneously measure rheology and WAXD enables a detailed study behind the physics of this surprising phenomenon. Indeed, the growth of the shear layer to considerable proportions coincides with an increasing pressure drop. Our results are in agreement with the observations of the Kornfield group, who found for comparatively mild flow conditions (shear stress of 60 kPa and shear times in the order of 10 s) a saturation of shish density in TEM\(^{27}\) and

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**Figure 1.** Azimuthal scans of the (110) diffraction of WAXD patterns (inserted) obtained with a) Pilatus detector and b) Frelon detector. Flow direction is vertical.

**Figure 2.** Pressure drop between the pistons for all piston speeds and flow times. Different colors and symbols indicate different flow speed and flow time, respectively.
In such conditions, it is conceivable that the volume fraction of crystalline material is large enough to alter the rheological properties on a macroscopic scale. In the current experimental results, however, the flow times are expected to be too short for the crystalline entities to grow to such proportions.

Analysis of the data confirms this expectation. Take $t = 0.2 \text{ s}$. The measurements with a piston speed of 120 mm s$^{-1}$ give a pressure drop of 550 bar; an increase of a factor 1.5 with respect to the steady state value at 0.1 s. Hence, on average, all the material in the entire slit has a viscosity of 1.5 times the viscosity of the melt. The space filling in the shear layer in the middle of the slit at this point in time is 5% (Figure 3b). We can estimate that such a volume fraction of perfectly aligned fibers would increase the modulus of iPP by a factor of 1.10.$^{[29]}$

The possibility of a percolating network formed by chains connecting shish is excluded; the radius of gyration of PP can be estimated by $R_g / M_w^{(1/2)} = 0.039 \text{ nm}$,$^{[30]}$ giving an average of $R_g = 23.5 \text{ nm}$ for the material in this study, while shish are typically 100–200 nm apart (Figure 4 and ref. [24]). Hence, a chain with average length will probably not form a link between shish. For our material, which is quite polydisperse, one could imagine that some chains on the high end of the molecular weight distribution are in fact long enough, but the material in the work from the Kornfeld group$^{[28]}$ is much less polydisperse. If the physics behind saturation of shish density in these experiments are the same, a percolating network can not be the cause of the viscosity upturn.

Based on the observations and the approximated quantification of the different effects, we can conclude that purely a suspension of shish would not affect the viscosity of the melt enough to explain the pressure drop observed.

Instead shish-kebabs must affect the melt rheology in a different way. We propose the following: some chains are partially inside the shish and partially inside the melt. Keller dubbed these chains “hairs,”$^{[6,31]}$ and hypothesized these crystallize subsequent to shish, forming the kebabs. We propose that these hairs interact with the surrounding melt and as a consequence cause a greater disturbance in the flow field around the shish than would have been the case if the shish were smooth.

**Figure 3.** a) Crystallinity averaged over thickness direction as determined from WAXD for all piston speeds and flow times, b) apparent crystallinity normalized by its value at $t = 100 \text{ s}$. Different colors and symbols indicate different flow speed and flow time, respectively.

**Figure 4.** Left: optical microscopy (OM) picture taken with crossed polarizers at the position of the windows for $v_{pist} = 140 \text{ mm s}^{-1}$ for 0.2 s. Right: TEM pictures taken at two locations separated by 350 µm in velocity gradient direction within the shear layer. Inserts show the Fourier Transforms of the TEM pictures. Indicated positions in the OM picture are approximate.
The following conceptual model is proposed to explain the experimental observations presented in this paper. Figure 5 serves as illustration, showing in the top row a schematic depiction of the morphology at a point somewhere along flow direction and in the bottom row shear stress and shear rate as a function of position along thickness direction. Time increases from left to right. Shortly after the start of flow, a flow field develops with high shear rate near the walls and zero shear rate in the center of the slit (Figure 5a). As a result, flow-induced nuclei appear; near the wall a large density appears, which quickly falls off going from the wall to the center of the slit. Near the wall, stretched chain segments attach to the existing nuclei forming shish (b). As material is continuously sheared, shish grow in length, increasing their volume fraction and, more importantly, increasing the total number of "hairs" that interact with the surrounding melt. At a certain point, their number becomes that large that the overall rheology of the material is macroscopically affected, causing a decrease in the deformation rate in the layer near the wall and an increase in the overall pressure drop (c). Because the deformation rate in the shear layer decreases, shish stop growing. Instead, because the total volumetric flow rate remains constant, the shear rate experienced by the material just outside the shear layer increases, causing the formation of shish (d) until the point where the increase in modulus hinders further shish growth (e–f), at which point the shear layer grows even thicker. This sequence of events continues until flow is ceased. Effectively, there is a front of shish-kebabs that propagates towards the center, with a layer with high density of point-like nuclei with constant density in front.

4. Conclusion

We have shown that the shish density within the shear layer formed in a slit flow geometry is independent of shear rate and shear time. A conceptual model is proposed to explain this observation, with the key ingredient that chains protruding from shish into the amorphous melt disturb the flow field around shishes. These macroscopically increase the modulus of the material and thus, at a certain density of shish, hinder further deformation and stop shish growth. Because volumetric flow rate remains constant, the material just outside the shear layer then experiences larger shear rates, causing shish to appear and the thickness of the shear layer to increase.

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More accurately, a precursor formed by flow which, if flow was ceased at an earlier time, would be so far away from other nuclei that it would be entirely covered by spherulitic overgrowth, see: H. Janeschitz-Kriegl, E. Ratajski, Colloid Polym. Sci. 2010, 288, 1525.


[23] For the measurement with piston speed 60 mm/s, the shear layer is too thin to give a signal in the frames with the short acquisition time.


[29] The generalized self consistent method gives the following expression for the modulus of a suspension of perfectly aligned fibers with concentration \( c \):

\[
\frac{G(c)}{G_{m}} = \frac{G_f(1+c) + G_m(1-c)}{G_f(1-c) + G_m(1+c)},
\]

with \( G_m, G_f \) and \( G \) the moduli of the matrix, the fibers, and the suspension in the direction in which the fibers are aligned, respectively. For a volume fraction of 5%, this yields \( G/G_m = 1.10 \) with \( G_m = 10^4 \) Pa and \( G_f = 10^6 \) Pa for iPP [18]. To get \( G = G_m = 1.5 \), we need \( c = 0.2 \). Alternatively, we might compare shish-kebabs to glass fibers, which are also much stiffer than the melt and typically have aspect ratios in the order of 100. Experimental data for such systems also show that volume fractions exceeding 10% are needed to give a viscosity increase of factor 1.5[32–36]. It takes the material near the windows 4 seconds to reach a space filling of 20%. Material upstream experiences faster structure formation, but this difference is not expected to be big enough to explain the pressure drop increase purely from a suspension of shish. The start-up time of the flow is 0.1 s, hence we can expect a time delay in flow history 0.05 s between material upstream and in the middle of the slit. Moreover, the pressure drop is 350 bar during the early stage of structure formation, giving a pressure difference between upstream and the middle of the slit of 175 bar, amounting to a depression in melting point of about 5 °C [37]. Neither of these effects are strong enough to accelerate crystallization enough to result in a space filling of 20% upstream already at 0.2 s.


