Structure evolution during film blowing

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Structure Evolution During Film Blowing: An Experimental Study Using In-situ Small Angle X-Ray Scattering

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Abstract

The on-line morphological development during film blowing of 2 different linear low density polyethylenes (LLDPE) and a blend of LLDPE with low density polyethylene (LDPE) has been investigated, for the first time, using synchrotron Small Angle X-Ray Scattering (SAXS). The processing conditions, blow-up ratio and take-up ratio, have been varied and the resulting lamellar thickness, linear crystallinity and orientation evolution in machine direction is obtained from a detailed analysis of SAXS data. Ex-situ SAXS and wide angle X-ray Diffraction (WAXD) confirmed the effect of molecular structure and composition on structure evolution observed in the on-line experiments. The results obtained provide a valuable set of data for the understanding of the film blowing process and can be used to extend and improve numerical model.

1 Introduction

Most plastic films and bags, ranging in sizes from sandwich bags to large films for agricultural uses, are made by the ingenious and engineering elegant process of film blowing. During this process a tubular film is extruded upwards through an annular die, blown up into a larger tubular film and cooled down by an external stream of cold air. The inflated, solidified tubular bubble is then flattened as it passes through the take-up rolls which also provide the axial tension needed to pull the film upward, and form an air seal so that a constant pressure, just above atmospheric, is maintained inside the bubble.

The process, although apparently simple, is rather complicated and challenging to understand: the solidifying polymer melt undergoes a combination of biaxial stresses and steep thermal gradients, leading to complex orientation, morphologies, and thereof properties, which are strongly dependent on the processing conditions used.

Another key issue concerns the tuning of final properties of the film by selecting the right material composition. For instance, polyethylene-based films are of great industrial relevance because of their relatively low production cost and easy processability: low density polyethylenes (LDPEs) were mostly used till a few decades ago because of their clarity, flexibility, sealing and barrier properties. Recent developments in metallocene-based synthesis techniques have brought into the market linear low density polyethylenes (LLDPEs) which show better mechanical properties and higher toughness. However LLDPEs show lower processability compared to LDPEs, such as high melt pressure and bubble stability, issues which are translated in surface irregularities causing high haze and loss of clarity [1, 2]. To overcome these drawbacks, LLDPEs are usually blended with a small amount (up to 10 % \text{wt}) of LDPE resulting in an improvement in processability at the expense of the final physical properties.

Extensive research has been carried out on the materials or on the final morphology of the blown films using a wide range of experimental techniques, such as X-ray scattering [3, 4], rheology [5, 6], electron microscopy techniques [7, 8], differential scanning calorimetry (DSC) [8] and FTIR trichroism [7]. Mostly off-line methods (also in industry) are used to modify the processing variables and material composition by trial and error until the optimal conditions are found. However, such a procedure is expensive and time consuming. A more systematic approach would be that of using data from real-time experiments to improve and validate already existing numerical models on the process [9, 10, 11, 12, 13]. In this way by applying these validated models the processing conditions could be modified a priori to get the desired properties. Despite the number of existing models, the amount of experimental data is far from being sufficient since only a few on-line studies were performed so far.
Moreover, the techniques used (wide angle X-ray diffraction, Raman spectroscopy, SALS and birefringence) were not able to study the structure evolution on a nano-scale while this is of fundamental importance, since mechanical and optical properties, including haze and clarity, are strongly dependent on morphological features such as lamellar thickness and crystalline superstructures, i.e. row nucleated structures, not detectable with the techniques just mentioned. To fill in this gap, the present paper focuses on the morphological development and evolution on a nano-metric length scale, in the range 1-100 nm using, for the first time, in-situ small angle X-ray scattering (SAXS). A well defined combination of machine settings as well as different materials are investigated in real time by mean of high energy synchrotron radiation, the structure evolution along the bubble from the die exit to well above the solidification line is provided and analyzed in detail. However, to confirm the on-line observation the final structure of the films is also analyzed by mean of ex-situ SAXS and WAXD measurements, the results were found in good agreement. Compared to previous on-line studies, we think we provide a set of well defined and reproducible experiments, as confirmed by the strain and strain rates analysis of experiments performed on different materials at the same combination of processing conditions. Our results are closer to real processing if compared to the several studies of Gururajan [14, 16] (blow-up ratios used of 0.6 and relatively low take-up ratios) and complementary to the studies of van Drongelen [15] and Bullwinkel [17] which employed WAXD and SALS, to investigate two completely different length scales. The main goal of this work is to demonstrate the feasibility of an on-line synchrotron SAXS study on film blowing and to provide experimental data that can be used to validate numerical models for this process.

2 Experimental

2.1 Materials

The materials used for this study are two commercial linear low density polyethylenes (named LLDPE 1 and LLDPE 2 in this work) and a blend of LLDPE 2 with 10%wt of low density polyethylene (LDPE), all provided by ExxonMobil. The two LLDPE grades, both prepared by metallocene catalysis, show similar molecular weight, different polidispersity indexes (PDI) and different amount of butyl-branching (6 and 2.1 %wt respectively) Another substantial difference between the two is the comonomer interchain distribution: LLDPE 1 has a relatively narrow unimodal interchain comonomer content distribution while LLDPE 2 has bimodal and broad interchain comonomer content distribution [19, 20]. Finally, the LDPE used for the blend has relatively higher molecular weight and polidispersity. The most important molecular features of the materials are listed in Table 1.

2.2 Film Blowing Setup

A Collin Blown Film Unit type 180-400 and extruder were installed at the Dutch Belgian Beamline BM26B at the European Synchrotron Radiation Facility (ESRF, Grenoble, FR). A picture of the setup is shown in Figure 1. The used die diameter and gap were 50 and 0.8 mm, respectively. Notice that the film blowing line is relatively small compared most blown film present in insustry. However, in this work we tried to use processing conditions as close as possible to the one used in ”real-life” processing.
<table>
<thead>
<tr>
<th>Material</th>
<th>$M_w$ [g mol$^{-1}$]</th>
<th>PDI</th>
<th>Butyl-branching [%wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE 1</td>
<td>94'000</td>
<td>3.9</td>
<td>2.1</td>
</tr>
<tr>
<td>LLDPE 2</td>
<td>108'000</td>
<td>2.4</td>
<td>6</td>
</tr>
<tr>
<td>LDPE</td>
<td>217'000</td>
<td>5.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1: Molecular characteristics for the materials used.

During film-blowing, two main quantities govern the stretch in the machine direction and the amount of expansion of the bubble (related to the stretch in transverse direction), the take-up ratio (TUR) and the blow-up ratio (BUR), respectively. The TUR is defined as the ratio between the pick-up speed at the take-up rolls and the average speed of the feed at the die exit, the BUR is given by the ratio between the final diameter of the bubble and the die diameter:

$$
TUR = \frac{v_{rolls}}{v_{die}} \quad BUR = \frac{D_{bubble}}{D_{die}}
$$

In order to have a direct comparison between the different materials used, the most important processing conditions were kept the same. The die extrusion temperature was set at 190°C and the extruder screw rpm, governing the feed, was kept constant for all the materials; in this way the thermo-mechanical history of the material leaving the die can be considered comparable for all the grades employed. Moreover, a set of four processing conditions was chosen using a combinatorial approach: for each of the two TUR used, two BUR were used. A complete overview of the processing conditions used is given in Table 2. The values of TUR and the position of the frost line were evaluated using the particle tracking method, according to the procedure described in the work of van Drongelen et al.[15], the BUR from "lay flat width" of the bubble produced.

Recently, similar experiments were done in our group, employing the same setup, but then coupled with in-situ wide angle X-ray diffraction[15]. Due to experimental problems at that time, related to the control of the cooling air flux from the air ring, the experiments were conducted in the absence of active air cooling, leading to a frost line at a large distance from the die, especially for the experiments at high take-up ratio. Consequently, X-ray patterns above the frost line for these conditions couldn’t be collected because of the limited extruder displacement (see Figure 2).

In this work, thanks to improvement made on the film blowing unit, cooling was achieved by using one cooling ring at which the air flow was adjusted till a stable bubble was obtained and, since then, the air flow was kept constant in order to have comparable conditions for all the experiments. The control of the air flow in a well controlled manner, also permitted to achieve a position of the frost-line much closer to the die exit and patterns below and above the frost line could be collected, permitting to follow the complete structure evolution for all experimental conditions. Moreover, due to an improved radial distribution geometry of the die a much better homogeneity of the frost line and of the thickness profile was achieved, significantly reducing the standard deviation and the experimental error on the X-ray patterns.
2.3 Strain and Strain Rates Calculation

As stated before, film blowing is a very complicated process and classifying the experiments just using BUR and TUR could be argued to be too rough. Hence, we provide an estimation of the local strain rates in machine and transverse direction by mean of fitting both the axial velocity profile and the bubble radius as a function of the distance from the die exit. The axial velocity profile was obtained by collecting videos of the bubble during processing for each condition and using the particle tracking method, as explained in detail in the work of van Drongelen[15]. The position of the tracker, in pixel vs. time, was converted into distance from the die exit vs. time using a calibration image. After calculating the derivative of the data, the axial velocity profile, $v_z$, was obtained and fitted with a sigmoidal function:

$$v_z(z) = a + \frac{b}{1 + e^{-\frac{z-c}{d}}}$$  \hspace{1cm} (2)

where a, b, c and d are fitting parameters and z is the distance from the die exit. Examples of the axial velocity profile fitting for the LLDPE 1 processed in two different conditions are presented in Figure 2.

The bubble shape, necessary to correctly evaluate strain rates in the two principal directions, was derived by image analysis of the frames from the videos used for particle tracking. After calibration of the image, i.e. conversion from pixel in distance, the coordinates of the bubble surface were extracted obtaining a description of the variation of the bubble radius, $R_z$, as a function of axial distance from
<table>
<thead>
<tr>
<th>Experiment</th>
<th>BUR [-]</th>
<th>TUR [-]</th>
<th>Troughput [g min⁻¹]</th>
<th>Frost line height [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LLDPE 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High TUR - High BUR</td>
<td>2.3</td>
<td>28.3</td>
<td>16.66</td>
<td>5.2</td>
</tr>
<tr>
<td>High TUR - Low BUR</td>
<td>1.7</td>
<td>28.3</td>
<td>16.66</td>
<td>12.0</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>2.4</td>
<td>8.7</td>
<td>16.66</td>
<td>8.6</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>1.8</td>
<td>8.7</td>
<td>16.66</td>
<td>11.6</td>
</tr>
<tr>
<td><strong>LLDPE 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High TUR - High BUR</td>
<td>2.3</td>
<td>28.7</td>
<td>16.14</td>
<td>4.5</td>
</tr>
<tr>
<td>High TUR - Low BUR</td>
<td>1.6</td>
<td>28.7</td>
<td>16.14</td>
<td>6.0</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>2.2</td>
<td>8.8</td>
<td>16.14</td>
<td>6.8</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>1.6</td>
<td>8.8</td>
<td>16.14</td>
<td>10.0</td>
</tr>
<tr>
<td><strong>LLDPE 2+10%wt LDPE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High - TUR High BUR</td>
<td>2.5</td>
<td>26.7</td>
<td>17.34</td>
<td>6.8</td>
</tr>
<tr>
<td>High - TUR Low BUR</td>
<td>1.4</td>
<td>26.7</td>
<td>17.34</td>
<td>11.4</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>2.5</td>
<td>8.2</td>
<td>17.34</td>
<td>6.4</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>1.5</td>
<td>8.2</td>
<td>17.34</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table 2: Experimental conditions for the three different materials used.

Figure 2: Velocity component along the machine direction as a function of the distance from the die for LLDPE 1 blown in two different conditions. The full lines represent the fitting obtained using Eq.2.

the die, $z$, according to Equation 3. An example of the fitted profile superposed to the corresponding image is presented in Figure 3.

$$ R_z(z) = e + f[1 - erf\left(\frac{z-g}{h}\right)] $$

(3)

where $e$, $f$, $g$ and $h$ are fitting parameters and $z$ is the distance from the die exit.
The axial velocity profiles, $v_z$, and the functions describing the bubble shape, $R_z$, obtained from video analysis were then used to calculate the strains and the strain rates along the machine and transverse direction. Expressions for these are given in Equations 4 and 5 for MD and TD, respectively:

$$\varepsilon_{MD} = \ln \frac{v_z}{v_0}$$
$$\varepsilon_{TD} = \ln \frac{R_z}{R_0}$$

$$\dot{\varepsilon}_{MD} = \frac{1}{v_z} \frac{dv_z}{dt} = \cos \theta \frac{dv_z}{dz} \tag{4}$$
$$\dot{\varepsilon}_{TD} = \frac{1}{R_z} \frac{dR_z}{dt} = \frac{v_z}{r} \frac{dR_z}{dz} \tag{5}$$

where $v_0$ is the axial velocity at the die exit, $R_0$ is the die radius and $\theta$ is the angle between the bubble surface and machine direction.

Examples of the strains and strain rates variations with distance from the die are provided in Figure 4 for two different experiments. The strain in both machine and transverse directions increases gradually until reaching a plateau value after the frost line when both velocity and radius of the bubble become constant. The gradient of deformation rates, both for MD and TD direction, increases until a maximum, where the highest expansion of the bubble takes place and then decrease to zero at higher distances, since both the radius and the axial velocity are constant and equal to their maximum value.

The effect of processing conditions, i.e. BUR and TUR, on the maximum strains and strain rates is summarized in Table 3. The maximum strains in machine direction at high take-up ratios are about double the maximum strains at low take-up ratios, while the strains in transverse directions double increasing the blow-up ratio. At high take-up ratios, the strain rates in machine direction are higher then the one in transverse direction by a factor between 2.5-4. At low take-up ratios, stresses and hence strain rates in transverse direction become higher and the relative ratio between the two decreases for the experiments conducted at high blow-up ratio, where the strain rates in the two principal directions are comparable. It is possible to appreciate that strains, strain rates in both directions and the related ratios between the 2, are comparable for the three different materials at the same processing condition (combination of TUR and BUR), confirming the good reproducibility of our experimental setup. Hence, the experiments presented in this work will be classified using blow-up and take-up ratios, since experiments performed in the same conditions of BUR and TUR are rather similar and then comparable.
Figure 4: Strains (a) and strain rates (b) along MD (full lines) and TD (dashed lines) as a function of the distance from the die exit for LLDPE 2 blend blown in two different conditions.

Table 3: Maximum strain rates achieved in machine direction (max \( \dot{\varepsilon}_{MD} \)), transverse direction (max \( \dot{\varepsilon}_{TD} \)) and relative ratios for all the performed experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( \dot{\varepsilon}_{MD}^{\max} ) [( \text{s}^{-1} )]</th>
<th>( \dot{\varepsilon}_{TD}^{\max} ) [( \text{s}^{-1} )]</th>
<th>( \dot{\varepsilon}<em>{MD}^{\max} / \dot{\varepsilon}</em>{TD}^{\max} )</th>
<th>( \dot{\varepsilon}<em>{MD}^{\max} / \dot{\varepsilon}</em>{TD}^{\max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High TUR - High BUR</td>
<td>2.08</td>
<td>0.87</td>
<td>2.39</td>
<td>1.95 / 0.69</td>
</tr>
<tr>
<td>High TUR - Low BUR</td>
<td>2.11</td>
<td>0.58</td>
<td>3.64</td>
<td>0.84 / 0.33</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>0.82</td>
<td>0.94</td>
<td>0.87</td>
<td>0.27 / 0.33</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>0.88</td>
<td>0.64</td>
<td>1.37</td>
<td>0.40 / 0.16</td>
</tr>
<tr>
<td>LLDPE 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High TUR - High BUR</td>
<td>2.08</td>
<td>0.88</td>
<td>2.33</td>
<td>1.45 / 0.63</td>
</tr>
<tr>
<td>High TUR - Low BUR</td>
<td>2.05</td>
<td>0.45</td>
<td>4.55</td>
<td>1.30 / 0.32</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>0.78</td>
<td>0.82</td>
<td>0.95</td>
<td>0.23 / 0.20</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>0.89</td>
<td>0.50</td>
<td>1.78</td>
<td>0.24 / 0.15</td>
</tr>
<tr>
<td>LLDPE 2+10%wt LDPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High TUR High BUR</td>
<td>2.07</td>
<td>0.97</td>
<td>2.13</td>
<td>1.50 / 0.46</td>
</tr>
<tr>
<td>High TUR Low BUR</td>
<td>2.12</td>
<td>0.43</td>
<td>4.93</td>
<td>0.83 / 0.36</td>
</tr>
<tr>
<td>Low TUR - High BUR</td>
<td>0.74</td>
<td>0.88</td>
<td>0.84</td>
<td>0.20 / 0.16</td>
</tr>
<tr>
<td>Low TUR - Low BUR</td>
<td>0.87</td>
<td>0.42</td>
<td>2.07</td>
<td>0.20 / 0.09</td>
</tr>
</tbody>
</table>

2.4 In-Situ X-ray Scattering Measurements and Data Analysis

The film blowing experiments were coupled with in-situ small angle X-ray scattering as shown in the schematic of Figure 5. Measurements were done using a X-ray source with a wavelength of 1.033 Å and a beam diameter of 300 \( \mu \)m. All SAXS patterns were collected using a Pilatus 1M detector (981×1043 pixels of 172 \( \mu \)m×172 \( \mu \)m placed at a distance of 5.162 m), an evacuated chamber was positioned...
between the bubble and the detector to reduce air scattering and absorption. The distance and tilt angle were calibrated using AgBe (silver behenate) as a standard. All X-ray images were corrected for the background scattering and normalized for synchrotron beam fluctuations using an ionization chamber placed before the sample and for the transmission of the film using a photodiode placed on the beamstop.

Since film blowing is a steady-state process, the structure evolution at different heights could be examined by raising the die and extruder step by step using a hydraulic lifter. In this way, 2D scattering patterns can be recorded at different heights, ranging from close to the die exit to beyond the solidification line, typically from 5 to 10 cm above. Measurements were done at least at 8 different positions, ranging from ~5 to ~25 cm from the die exit, depending on the position of the frost line. To achieve a better statistics, 10 SAXS patterns were acquired in each position with an exposure time of 10 s resulting in a total acquisition time of 100 s. The sample to detector distance was chosen long enough so that the intensity scattered from both the sides of the bubble superposed and the resulting 2D SAXS patterns could be considered as an average of the front and back side of the bubble (see Appendix 1).

![Figure 5: Schematic of the film blowing device combined with in-situ small angle X-ray scattering.](image)

Two type of reduction of the 2D SAXS patterns to 1D profiles were performed, as shown in Figure 6, using the Fit2D software package (ESRF, France). The 1D profiles of intensity \( I \) versus scattering vector \( q \), where \( q = \frac{4\pi}{\lambda} \sin\theta \) and \( \theta \) half of the scattering angle, were obtained from a radial integration on a slice of the meridional scattering region of the SAXS pattern (Figure 6a). 1D azimuthal intensity profiles \( I(\phi) \) of the 2D SAXS patterns were obtained by averaging the intensity over a small \( q \) region centered around the value of the peak in the radial intensity profile (Figure 6b).

It is widely recognized that the preferred approach to calculate the lamellar crystal and amorphous layer thicknesses from SAXS data of uni-axially oriented samples is the projection method [21] which uses the following formalism:

\[
I_1(q) = \int_0^\infty I(q_{12}, q_3)q_{12}dq_{12}
\]  

(6)
Where $I_1$ is the integrated intensity along the meridian, $q$ is the scattering vector, the subscript 3 represents the meridional direction and the subscript 12 the equatorial direction. Since the measured 2D SAXS patterns showed large variations in orientation, depending on the material and conditions used, and never a completely uniaxially orientated pattern was observed, the 1D meridional intensity was analysed as for an isotropic system [22, 23], using the conventional “sliced” method as proposed by Hsiao et al. for the analysis of heat-drawn polyamide-6,6 fibers [24] and Heeley et al. [25] for tape extrusion of polyethylene tapes. Consequently the intensity profile were corrected by a Lorenz factor and the residual background intensity due to thermal density fluctuations ($I_b$) was subtracted according to the procedure suggested by Ruland [26] and implemented by Vonk [27]. The data were then extrapolated to $q \to \infty$ according to the Porod’s law:

$$\lim_{q \to \infty} [I(q) - I_b] = K_P q^{-4}$$

(7)

where $K_P$ is the Porod’s constant. The extrapolation to $q \to 0$ was carried out using the Debye-Beuche equation [28]:

$$\lim_{q \to 0} [I(q) - I_b] = \frac{B}{(1 + C^2 q^2)^2}$$

(8)

where $B$ and $C$ are interpolation parameters.

Using these extrapolations, the normalized self-correlation function $\gamma(r)$ was calculated according to [21, 23]:

$$\gamma(r) = \frac{\int_0^\infty [I(q) - I_b] q^2 \cos(qr) dq}{\int_0^\infty [I(q) - I_b] q^2 dq}$$

(9)

where $r$ is the coordinate in the real space.

From the main correlation triangle and the secondary maximum of the autocorrelation function (see Fig 4b) the average values of lamellar thickness ($l_c$) and long period ($L$) were evaluated as shown in Figure 7. The index of linear crystallinity was then evaluated by the ratio between the lamellar thickness and the long period ($x_{lin} = l_c/L$).
Figure 7: (a) Example of Lorentz corrected 1D intensity: open circles are the experimental data, the full blue line and the dashed red line represent the extrapolations at low and high q using Debye-Beuche and Porod law, respectively. (b) Corresponding normalized auto-correlation function: the red circles represent the calculated values of lamellar thickness ($l_c$) and long period ($L$).

Finally, azimuthal scans obtained from the azimuthal integration presented in Figure 6b were fitted with a Lorentzian function as shown in Figure 8 and the reciprocal of the full width at half maximum (1/FWHM) was used as a measure for the degree of orientation. More oriented samples will show a narrower azimuthal intensity distribution and thus higher values of 1/FWHM. Since in few cases the patterns showed a shift of the maximum in intensity with respect to the meridian ($\phi = 0$) because of a slight experimental misalignment of the film with the machine direction, the azimuthal SAXS intensity distribution was corrected before performing any analysis.

Figure 8: Azimuthal scattering profile (open circles) of SAXS data fitted using a Lorentzian function (full red line) to evaluate the FWHM.
2.5 Ex-situ SAXS/WAXD analysis

Ex-situ X-ray measurements were performed at the Dutch-Belgian (DUBBLE) beamline BM26 of the European Synchrotron Radiation Facility (Grenoble, France) using a wavelength of 1.033 Å. A Pilatus 1M detector placed at a distance of 2.727 m and a Frelon 2K CCD camera (48.8 µm x 48.8 µm) at 0.139 m were employed to record SAXS and WAXD two-dimensional patterns, respectively. The acquisition time per image was set to 10 s both for SAXS and WAXD and each pattern was corrected for beam intensity and scattering of the empty sample cell. The SAXS images were analyzed as explained in Section 2.4 to obtain linear crystallinity, lamellar thickness and a measure for the orientation (1/FWHM). WAXD images were processed with the software package FIT2D to obtain intensity versus scattering angle (2θ) profiles. Crystallinity was calculated after deconvolution of the total intensity scattered by the crystalline ($A_{\text{crystal}}$) and amorphous ($A_{\text{amorphous}}$) domains:

$$X_{\text{WAXD}} = \frac{A_{\text{crystal}}}{A_{\text{crystal}} + A_{\text{amorphous}}} \times 100$$

(10)
### 3 Results and Discussion

To separate the influence of processing conditions from those of the molecular composition of the three materials used in this work, the results in this section are first briefly explained in a qualitative way by analysing the 2D SAXS patterns; then the quantitative analysis is presented twice: first highlighting the difference between the different processing conditions and later analysing the effect of the material composition. Moreover the values of the morphological characteristics calculated from SAXS data (linear crystallinity, orientation and lamellar thickness) for the final films are shown as horizontal lines in the right side of the plots in Figures 11 - 16. These will be discussed in detail in Section 4 of this paper.

#### 3.1 Qualitative analysis of 2D SAXS data

2D SAXD patterns collected in a distance range from just above the frost line to the highest reachable distance from the die exit for the three different materials used and for different combinations of TUR and BUR are shown in Figure 9. All the patterns were averaged over the 10 different frames collected at the same position, i.e. distance from the die exit, machine direction is vertical. It is evident that the scattering patterns and hence the morphologies on a nano-metric length scale are strongly influenced by both the processing conditions and the material composition. Moreover, these results show clearly the substantial structural changes above the frost line, i.e. after solidification. For the interpretation of the results, Figure 10 gives a schematic presentation of typical 2D SAXS patterns and related morphologies for semicrystalline polymers having different degree of orientation.

LLDPE 1, with higher polydispersity and narrow unimodal comonomer content distribution, shows rather oriented patterns at high take-up ratios: close to the frost line some diffuse scatter polarized in the meridional region is observable for both high and low BUR, although no clear interference peak is present: lamellae with a long correlation distance start to form with their normal parallel to the machine direction. At high BUR, this evolves into two distincts lobes polarized at the meridian, indication of regularly spaced stacks of lamellae with their normals parallel to machine direction as represented in Figure 10 e. At low BUR, the clear shape of tear drop pattern is present indicating a lamellar morphology with normals in machine direction and with a broader distribution of spacing and thickness (Figure 10 d). At low take-up ratios both for high and low BUR, the diffuse scatter in the meridional region close to the frost line develops further away from it (23 cm from the die exit) into a two lobes pattern superimposed on some obvious radial scattering: stacks of lamellae oriented in machine direction are mixed with randomly oriented crystals (Figure 10 a and e).

The second linear low density polyethylene studied, LLDPE 2, having lower polydispersity and a broad bimodal comonomer content distribution, shows less oriented SAXS patterns. At high take-up ratios, close to the frost line small meridional lobes with a big correlation distance are present. These develops into broader meridional lobes superimposed to a clear scattering ring further away from the frost line: stacks of oriented lamellae are mixed with lamellae without any preferential orientation (Figure 10 a and e). At low take-up ratios a rather isotropic scatter is observed close to the frost line that changes into meridional arcs superposed to Debye-Sherer rings (Figure 10 a and b), indicating a rather low orientation of lamellae’s normals along machine direction.

Finally, blending LLDPE 2 with 10%wt of LDPE has a huge effect on the morphology. At high take-up ratios and close to the frost line the typical scattering feature of meridional streaks (Figure 10 c)
is observed: stacks of lamellae with small lateral size and different thickness are highly oriented in machine direction, away from the frost line the patterns evolve into tear drop shaped scattering lobes (Figure 10 d): lamellae are well oriented in machine direction but their spacing and thickness is not homogeneous. At low take-up ratios the morphology is rather different for high and low blow-up ratios. For high BUR the pattern presents meridional lobes that become more evident moving away from the frost line. For low BUR a rather diffuse scattering pattern is observed in the meridional region at the frost line. At 22 cm away from the die a rather small meridional interference peak appears, indicating the presence of few oriented lamellae with small lateral sizes and a broad distribution of long periods and thickness.
Figure 9: Representative 2D SAXS patterns for the three materials and the four processing conditions used, the distance from the die exit of each pattern is indicated on top. The misalignment of some of the patterns with the meridian (LLDPE 2 at high take-up ratios) is due to a tilt of the film-blower in respect to the beam. Machine direction is vertical.
3.2 Effect of processing conditions

3.2.1 Linear crystallinity evolution

Crystallization of polymers during processing is a complicated process, influenced by multiple variables, as cooling rates, flow fields and pressure, and most often by a combination of them. During film blowing two main quantities play a major role: the degree of cooling, dictated by the film thickness and the air flow, and the molecular orientation, dominated by the stresses in machine direction. For example, higher blow-up ratios imply thinner films and consequently higher (average) cooling rates while higher take-up ratios increase the stresses in machine direction forming row nuclei that can promote crystallization kinetics. For the reader’s convenience, the evolution of crystallinity is presented here in two different ways in figure 11: as a function of the distance from the die exit (a, c, e) and of the time elapsed since the melt left the die (b, d, f). The spatial evolution describes the structure evolution along the bubble, the time evolution the crystallization kinetics.

The spatial evolution of the linear crystallinity as a function of the distance from the die exit for all combinations of BUR and TUR used is presented for the three different materials in Figure 11 a, c and e. For all the grades and for the selected processing conditions, it is clear that the processing parameter dictating the crystallization evolution along the bubble is the BUR: higher blow-up ratios and hence thinner films undergo higher cooling rates (for a constant air cooling flow) and consequently solidify closer to the die exit.

While the effect of BUR on the spatial evolution is evident, no clear trend can be found for the take-up ratio. The time evolution of crystallinity is more instructive in this respect, as becomes clear from Figure 11 b, d and f, at same value of BUR independently of the material used the film crystallizes faster when the take-up ratio is higher: this is evidence that axial stresses have an influence on the solidification process inducing row nuclei that strongly accelerate crystallization kinetics.
It is also worth noting that the frost line does not mark a clear boundary between the melt and the crystalline state: the linear crystallinity has values of about 15-20 % around the frost line and further increases along the bubble vertical direction, reaching, eventually, a plateau level of 30 % for almost all materials and processing conditions.

It is common practice to address the frost line as the melt to solid transition since the radius of the bubble becomes constant, i.e. the film becomes rigid. Moreover the film often undergoes a loss of clarity (haziness) since the crystal superstructures (spherulites or row-nucleated structures), or the heterogeneities of the film, reach dimension similar or bigger than the wavelength of visible light, which is therefore scattered causing the loss of transparency. Nevertheless this does not mean that solidification is finished, crystallization can still proceed further away from the frost line as observed in this work and in other on-line experiments [15, 16]. This is even more relevant in this work where linear low density polyethylenes are employed: it is well known that branched polymers exhibit a large amount of secondary crystallization in non-isothermal conditions [29, 30, 31, 32] since longer crystallizable sequences fold into lamellae at higher temperature while the shorter ones crystallize at lower temperatures. For these materials the relative amount of secondary crystallization can reach values as high as 50 %: it appears then reasonable to address the increase of crystallinity observed after the frost line mostly to secondary crystallization.
Figure 11: Evolution of the linear crystallinity for LLDPE 1 (a, b), LLDPE 2 (c, d) and the blend of LLDPE 2 and 10%\textsubscript{wt} of LDPE (e, f) as a function of the distance from the die exit (a, c, e) and time from the air ring (b, d, f) for the four processing conditions used. Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of linear crystallinity for the final films.

3.2.2 Orientation evolution

As already explained in Section 2.4, the reciprocal of the full width at half maximum of the azimuthal intensity distributions (1/FWHM) is used in this work as an indicative measure of the degree of lamellar orientation in respect to machine direction. The results for the three different grades and for
all processing conditions are presented in Figure 12.
In contrast to what was observed with the crystallinity evolution, the TUR has a major influence on the
degree of lamellar orientation, especially the blend shows this effect clearly. Two different phenomena
can be recognized: for LLDPE 1, LLDPE 2 and for the blend processed at low take-up ratios, the
orientation reaches rather constant values immediately after the frost line as already observed by Van
Drongelen et al. [15], whereas the the blend at high TUR shows a decrease of the orientation moving
away from the frost line. In the first case, stacks of lamellae from the melt oriented in machine
direction, their orientation being proportional to the stresses applied in machine direction (depending
on the take-up ratio). In the case of the blend processed at high TUR, i.e. higher stresses in machine
direction, few oriented row-nucleated structures with lamellae small in lateral size form at the frost line.
This is evident from the meridional streaks observed in the 2D SAXS patterns (Figure 9), where the
lateral growth of lamellae from these structures causes the observed decrease in orientation. There is
no clear effect of the previously discussed secondary crystallization on the overall orientation, probably
because the insertion of thinner lamellae happens within the template of already formed and oriented
primary lamellae resulting in a rather constant orientation.

Figure 12: Evolution of the reciprocal of the full width at half maximum (1/FWHM) as a function of
the distance from the die exit for LLDPE 1 (a), LLDPE 2 (b) and the blend of LLDPE 2 and 10%wt
of LDPE (c) for the four processing conditions used. Vertical dashed lines represent the position of the
frost line. The horizontal full lines on the right side of the graphs represent the values of 1/FWHM for
the final films.
3.2.3 Lamellar thickness evolution

The spatial evolution of lamellar thickness along the bubble is presented in Figure 13 for the two LLDPEs (a, b) and for the blend (c) for the four combinations of processing conditions. Also in this case, the processing parameter governing the lamellar thickness evolution along the bubble is the BUR: for all the materials used lower blow-up ratios and hence thicker films/slower cooling rates translate into slightly higher lamellar thickness. Moreover, a decrease of the average lamellar thickness is observed moving away from the frost line. As already stated before, this can be explained in terms of secondary crystallization: thinner lamellae, constituted by shorter linear sequences and therefore requiring higher undercoolings to crystallize, insert between the template of thicker primary lamellae formed close to the frost line. As a result the average lamellar thickness decreases while gradually thinner lamellae crystallize far from the frost line.

Figure 13: Evolution of the lamellar thickness as a function of the distance from the die exit for LLDPE 1 (a), LLDPE 2 (b) and the blend of LLDPE 2 and 10% wt of LDPE (c) for the four processing conditions used. Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of lamellar thickness for the final films.
3.3 Effect of material composition

3.3.1 Linear crystallinity evolution

The crystallinity spatial evolutions along the bubble is presented for all materials per processing condition in Figure 14. As already explained at the beginning of this section, these are the same results shown in Figure 11 a, c and e, but presented in a way that highlights the effect of the different molecular characteristics of the grades used in this work.

It appears clearly that the effect of the material composition on the crystallinity evolution along the bubble is not as evident as the one of the processing conditions. At high blow-up ratios (Figures 14 a and c) there are no clear differences between the three material used: crystallinity increases gradually moving along the bubble away from the frost line and reaches constant values of about 30 % for all grades. At low blow-up ratios (Figures 14 b and d) the blends start to crystallize at a higher position compared to the two LLDPEs, consequently the full spatial evolution of the linear crystallinity could not be captured because of experimental limitation related to the displacement of the extruder and the die.

Flory’s phase equilibrium theory permits to evaluate the equilibrium melting of copolymers under the assumption that co-units (branching) are excluded from the crystal lattice [33]. According to this theory, the equilibrium melting temperature of the copolymer, $T_{0m_{corpo}}$, related to the one of the homopolymer, $T_{0m}$, can be expressed as:

$$\frac{1}{T_{0m}} = \frac{1}{T_{0m_{corpo}}} + \frac{R}{\Delta H_u} \ln p$$

(11)

Where, $\Delta H_u$ is the enthalpy of fusion per mole of crystalline repeating unit, and $p$ is the crystallizable sequence propagation probability. In the case of statistical copolymers, $p < 1$, and a large depression of the equilibrium melting of copolymers is predicted. If this is translated in terms of undercooling $\Delta T = T_{m}^0 - T_{exp}$, it appears clear that a material with a higher comonomer content requires lower $T_m^0$ in order to crystallize. When the cooling rates and hence the undercooling are high enough, as in the case of thinner films at high blow-up ratios (see Figures 14 a and c), all the materials can crystallize rather close to the die exit (about 15 cm). At low blow-up ratios, when the films are thicker and the cooling rates slower, the effect of the comonomer content is evident: LLDPE 1, with the lowest comonomer content, crystallizes closer to the die exit, followed by LLDPE 2 and the blend.
Figure 14: Evolution of the linear crystallinity as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of linear crystallinity for the final films.

3.3.2 Orientation evolution

The evolution of the reciprocal of the FWHM is presented in Figure 15 a-d for the four processing conditions used comparing the three different materials in each graph. The LLDPE with a lower comonomer content and a narrow interchain comonomer distribution (LLDPE 1) always show a relatively higher orientation than LLDPE 2, having higher comonomer content and broad bimodal comonomer distibution. The effect of blending the LLDPE 2 with LDPE on the overall orientation in machine direction is also clear: the blend always shows the highest orientation and at high take-up ratios it presents value of $1/FWHM$ up to 4 times higher than the neat material.

The difference between the two LLDPEs can be explained in terms of relaxation times: although they have about the same molecular weight, the polydispersity of LLDPE 1 is about 2 times higher, suggesting an higher molecular weight tail that has higher relaxation time and hence promotes the formation of row nuclei on which oriented lamellar structures can grow. It is well known that for flow induced (row) nucleation the high molecular weight tail is dominant [34, 35, 36]. The bigger increase in orientation of the blend can be explained in the same way: the LDPE used has a molecular weight
twice bigger than LLDPE 2 (217'000 vs 108'000 g mol$^{-1}$) and an even bigger polydispersity (5.9 vs 2.4); the longest chains can stay stretched longer and induce oriented morphology.

Figure 15: Evolution of the full width at half maximum (1/FWHM) as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of 1/FWHM for the final films.
3.3.3 Lamellar thickness evolution

The lamellar thickness evolutions along the bubble are plotted in this subsection for each individual experimental condition, comparing the three different materials in Figure 14 a-d. Values between 4 - 5.5 nm are found for all the materials and the processing conditions, in agreement with typical values found in literature for LLDPEs at high supercoolings [37, 38]. Some differences are observed at high take-up ratios: in this processing conditions, the blend always show the larger thickness, followed by LLDPE 1 and LLDPE 2. The lamellar thickness evolution shows the same trends of the orientation evolution: as stated before, the blend showed the highest orientation at high TURs, followed by LLDPE 1 and LLDPE 2.

It is well known that row nuclei, created by shear or elongational flow, can not only produce oriented structures but also promote crystallization kinetics by increasing the nucleation density of orders of magnitude [36]. Consequently, when these precursors are present the undercooling required to crystallize is lower, hence the lamellar thickness is higher.

![Graphs showing lamellar thickness evolution](image)

Figure 16: Evolution of the lamellar thickness as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of lamellar thickness for the final films.
4 Final Structure and Morphology of the Films

The values of linear crystallinity ($x_c^{(SAXS)}$), lamellar thickness ($l_c^{(SAXS)}$), reciprocal of the full width half maximum of the SAXS peak (1/FWHM) and crystallinity from WAXD evaluated from X-ray data analysis for the films collected at the winder, after the take-up rolls, are presented in Table 4. The values of crystallinity calculated from WAXD are in good agreement with the ones evaluated from SAXS autocorrelation function, confirming the goodness of our analysis.

Values of linear crystallinity slightly higher (up to 10% for the blend at low BUR) than the ones recorded at the highest reachable position from the die exit are found for all the materials and experimental conditions. As already stated before, this is a clear indication that the material can continue the crystallization process also well above the frost line, not only close to the die but also just below the take-up rolls where it further cools down. This observation is in agreement with the fact that the average values of lamellar thickness are significantly lower (0.5 to 1 nm) than the one recorder at the highest position during the on-line experiments. The increase in crystallinity out of our experimental observation window involves the insertion of thinner lamellae, resulting in a final smaller average lamellar thickness [32].

Differently from crystallinity and lamellar thickness, the values of orientation for the final films does not change drastically compared to the ones collected in-situ far at the biggest distance from the die exit. As already discussed in Section 3.2.2, the secondary crystallization does not affect the overall orientation probably because gradually thinner lamellae insert between thicker crystals and their orientation is governed by the orientation of the pre-existing crystals template.

<table>
<thead>
<tr>
<th></th>
<th>$x_c^{(SAXS)}$</th>
<th>$l_c^{(SAXS)}$</th>
<th>1/FWHM$^{(SAXS)}$</th>
<th>$x_c^{(WAXD)}$</th>
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<tr>
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<td></td>
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<td></td>
<td></td>
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<td>0.010</td>
<td>28</td>
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<td>LLDPE 2</td>
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Table 4: Relevant morphological parameters of the final PE films evaluated from ex-situ SAXS and WAXD data.
5 Conclusions

The effect of processing conditions and of material composition on structure development during film blowing was investigated using for the first time in-situ SAXS. Linear crystallinity, lamellar thickness and orientation spatial evolution were evaluated as a function of the distance from the die exit for a set of 4 processing conditions and 3 different materials. It has been demonstrated that the blow-up ratio is the parameter dominating the crystallinity and lamellar thickness spatial evolution, since it controls the film thickness and the consequent cooling rates/undercoolings experienced along the bubble. Differently, orientation is dictated by the take-up ratio, via control over the stresses in machine direction and the possibility to form row nucleated structures. For the selected materials, solidification can proceed well above the frost: it was observed that linear crystallinity increases for about 50%, orientation stays constant and the average lamellar thickness slightly decreases due to formation of thinner lamellae at higher undercoolings along the bubble in machine direction.

It was observed that higher comonomer content causes the material to crystallize more far away from the die exit at higher undercoolings and hence forming thinner lamellae. Blending LDPE in a matrix of LLDPE increased orientation of a factor 4 at high TUR and increased the lamellar thickness because of formation of row nucleated structures at lower undercooling, close to the die exit. Ex-situ X-ray analysis on the final films morphology permitted to get the final values of morphological parameters and confirmed the trend of the results observed during the on-line experiments.

This set of data is the first on-line study on the film blown process using small angle X-ray scattering. It can be used to understand and control the process, and with that the final properties, and validate and improve already existing numerical models.

6 Acknowledgments

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Appendix 1

Before performing the SAXS measurements we made sure that the distortion of the scattered patterns due to the bubble curvature below the frost line was negligible. The beam size employed was 300 microns and the highest curvature of the bubble observed was 0.8. To confirm that the curvature effects are negligible the integrated intensities obtained from the top and bottom quadrants of the scattered SAXS image collected below the frost line and close to the curvature are presented in Figure 17. It is possible to appreciate that the two patterns superpose in the entire q range, except at very low angles due to beamstop asymmetry and at q of about 0.15 and 0.35 due to the gap between different section of the detector (see inset in Figure 17).

We performed a simple calculation in the situation where the diameter of the bubble is 12 cm (related
Figure 17: SAXS integrated intensity obtained from the bottom (full line) and top (dotted line) quadrants for a pattern collected close to the curvature of the bubble for the experiment performed with LLDPE1 at High TUR and High BUR. The inset represent the 2D SAXS pattern for the same experiment.

to the highest BUR) and the typical long period is 15 nm. This would lead to a shift of about 5 pixels at the Pilatus detector for the scattering peak generated from the different walls of the bubble. The peak broadening due to the long period distributions ranges from 50 to 100 pixels, the effect is then negligible.
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Evolution of the linear crystallinity for LLDPE 1 (a, b), LLDPE 2 (c, d) and the blend of LLDPE 2 and 10% wt of LDPE (e, f) as a function of the distance from the die exit (a, c, e) and time from the air ring (b, d, f) for the four processing conditions used. Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of linear crystallinity for the final films. 

Evolution of the reciprocal of the full width at half maximum (1/FWHM) as a function of the distance from the die exit for LLDPE 1 (a), LLDPE 2 (b) and the blend of LLDPE 2 and 10% wt of LDPE (c) for the four processing conditions used. Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of 1/FWHM for the final films. 

Evolution of the lamellar thickness as a function of the distance from the die exit for LLDPE 1 (a), LLDPE 2 (b) and the blend of LLDPE 2 and 10% wt of LDPE (c) for the four processing conditions used. Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of lamellar thickness for the final films. 

Evolution of the linear crystallinity as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of linear crystallinity for the final films. 

Evolution of the full width at half maximum (1/FWHM) as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of 1/FWHM for the final films. 

Evolution of the lamellar thickness as a function of the distance from the die exit for the three materials processed using high TUR - high BUR (a), high TUR - low BUR (b), low TUR - high BUR (c) and low TUR - low BUR (d). Vertical dashed lines represent the position of the frost line. The horizontal full lines on the right side of the graphs represent the values of lamellar thickness for the final films. 

SAXS integrated intensity obtained from the bottom (full line) and top (dotted line) quadrants for a pattern collected close to the curvature of the bubble for the experiment performed with LLDPE1 at High TUR and High BUR. The inset represent the 2D SAXS pattern for the same experiment.