DUBBLE – EXPERIMENT REPORT

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Beamline: BM26-B	Date(s) of experiment: 15/12/2014 – 17/12/2014	Date of report: 12/2/2015
Shifts: 12	Local contact(s): G. Portale	

1. Who took part in the experiments?

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Were you able to execute the planned experiments?

YES. As explained in detail later in this report, a good set of experiment was performed thanks to the modifications to the experimental setup.

2. Did you encounter experimental problems?

NO.

3. Was the local support adequate?

YES. The support of the local contact, G. Portale and the technical staff, was needed to accurately set up the experimental equipment. Moreover, they were able to solve problems related to the triggering of the detectors, indispensable for the fast acquisition mode, and to fix the bug relative to simultaneously acquire fast and slow diffraction patterns.

4. Are the obtained results at this stage in line with the expected results as mentioned in the project proposal?

YES. A set of in situ X-ray/extensional rheology experiments on an isotactic polypropylene (iPP) supplied by Sabic was already performed in July 2014. Unfortunately the limits of the experimental setup compromised the success of the measurements: the main problems were related to the old material used for the oven windows (Kapton) which presents two diffuse halos in the wide angle region, as typical for amorphous polymers. The signal/background ratio was extremely small and consequently the data analysis of frames acquired in fast acquisition mode was impossible.

A significant improvement to the oven design was made in the workshop of mechanical engineering department at TU/e substituting Kapton with Mica, which is completely transparent to X-Rays both at wide and small angle.

The handling of the window was also made much more practical and now the sample mounting time has been significantly reduced, preventing heat loss.

The same set of experiments has been repeated using the new modified setup (Figure 1). This time we were able to collect processable X-ray data, also with an acquisition frequency of 30 frames/s during very short flow times, making possible the main aim of our work which is correlate rheology and crystallization behavior.

Figure 1. Picture of the new modified setup for coupled extensional rheology/in-situ X-rays installed at the synchrotron in Grenoble.

The experimental protocol adopted consists in holding the sample at 220°C for 10 mins to erase all thermo-mechanical history and subsequently cooling down to the experimental temperature (T_{ext}) of 135°C. After a stabilization time of 5 minutes at T_{ext} a Hencky strain (ε_H) of 3.5 (maximum achievable with the experimental setup) was imposed to the polymer melt at a certain Hencky strain rate ($\dot{\varepsilon}_H$) as depicted in the schematic drawing in Figure 2.

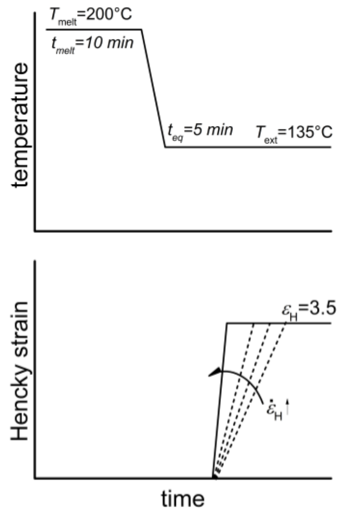


Figure 2. Experimental protocol used for the extensional rheology experiments.

Transient uniaxial elongational viscosities (η_e) at strain rates ranging from 5–25 s^{-1} are given in Figure 3. The dotted line represents the transient elongational viscosity 3η(t) of the linear viscoelastic envelop (LVE). The deviation from LVE at higher strain is clear once a certain critical value of the strain (ε_H=3) is exceeded. These nonlinear effects can be directly related to crystallization during flow and our aim was to capture this phenomenon in situ using high frequency detectors (30 frames/s) present at DUBBLE.

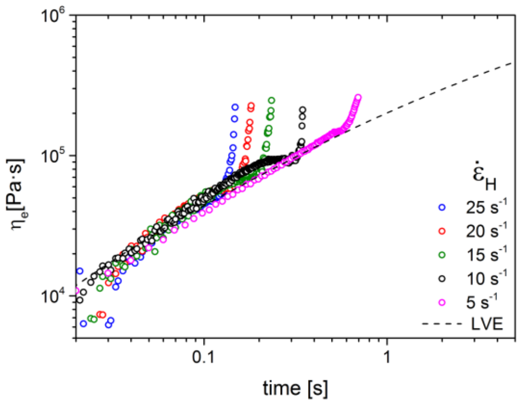


Figure 3 Tensile stress growth curves for an iPP grade over a range of Hencky strain rates measured at temperatures of 135°C (open circle).The dotted line represents the linear viscoelastic envelope.

Combined WAXD/SAXS experiments allow to investigate both the crystal structure and the morphological evolution.

Since in our experiments two crystal polymorphs of iPP were observed (α and β), two characteristic reflections diffracted at wide angle were taken as a measure of the amount of different crystals: the (110) and the (300) for the α and β form, respectively. After subtraction of the isotropic contribution of the amorphous scattering, a Lorentzian function was used to fit the two peaks indicated by the arrows in Figure 4(a).

Regarding SAXS patterns analysis, since the expected shish-kebab morphology presents anisotropic scattering, three azimuthal regions were defined to separate the intensity scattered by rod-like structures parallel to flow direction (shish) from the one scattered by stacks of lamellae oriented in the direction perpendicular to flow (kebabs). A diagonal region was defined to quantify a contribution to the scattering from isotropic structures (i.e. spherulites) that may occur during isothermal crystallization. The definitions adopted in this report are given in Figure 4(b).

The integrated intensities in the three different azimuthal regions were defined as:

$$I_{SAXS} = \int_{q_{min}}^{q_{max}} \int_{\phi_{min}}^{\phi_{max}} I(\phi, q)\, d_{\phi} d_{q}$$

where $q=(4\pi/\lambda)\sin(\theta)$ is the scattering vector, ϕ the azimuthal angle, q_{min} and q_{max} are the minimum and the maximum values of q experimentally accessible and ϕ_{min} and ϕ_{max} the minimum and the maximum values of ϕ for the chosen azimuthal region.

The values of q corresponding to the maximum of the scattering peaks of the integrated meridional intensities (q^*) were determined after application of Lorentz correction and background subtraction. The long period between the adjacent kebab stacks, L_P, was evaluated by simply applying Bragg's law, $L_P = 2\pi = q^*$.

(a) (b)

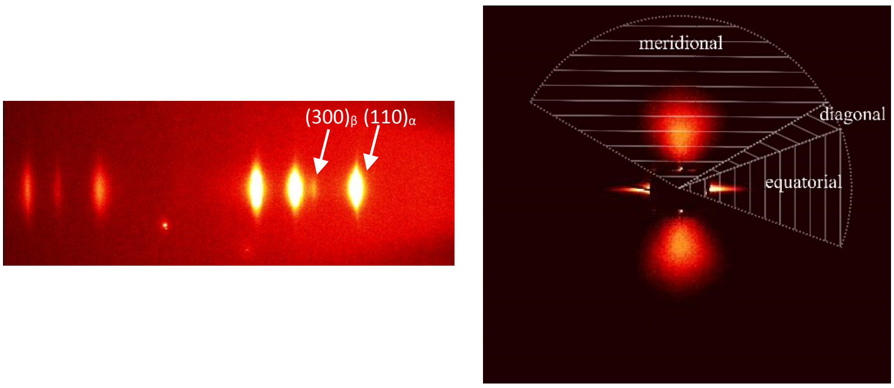
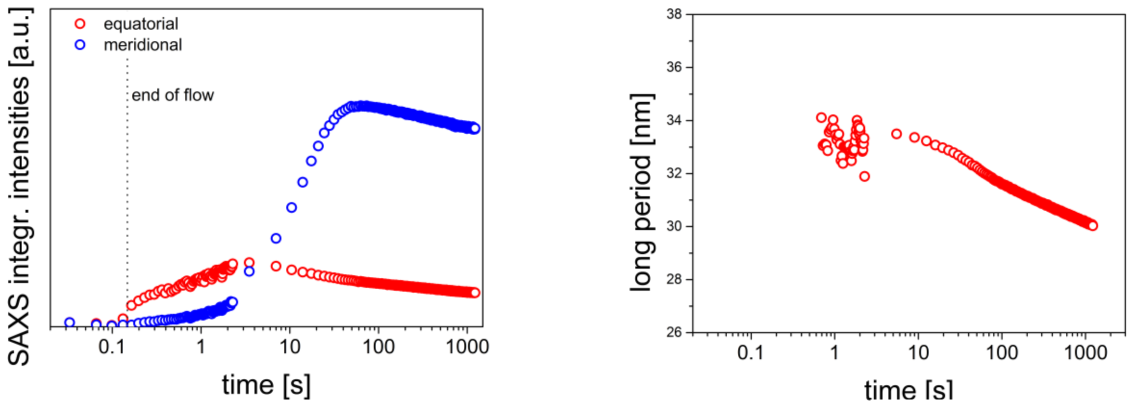


Figure 4 Typical WAXD (a) and SAXS (b) patterns for the extensional rheology/ in-situ X-Rays experiments.

Time evolutions of equatorial and meridional intensities for the experiment performed with the highest strain rate are presented in Figure 5(a). Equatorial intensity, related to scattering of extended chain crystals aligned along the flow direction, starts to increase at Hencky strain of about 3, suggesting that the deviation from linearity observed in rheology can be related to the formation of a shish "network".

During the isothermal crystallization after flow the equatorial intensity continues to increase for about 3 seconds indicating the growth of shish structures; at the same time meridional intensity shows a slight increase, indicating nucleation of lamellar stacks on the shish cores. In about 40 seconds both the meridional and the equatorial intensities reach a maximum value and then show a small decrease during the 20 minutes time observation window. An analysis of the long period evolution, shown in Figure 5 (b), suggests that during the same time interval kebabs start interdigitating causing a decrease of the average distance between one lamella and the other (long period) and a loss of contrast in the direction perpendicular to flow which causes the decrease observed in meridional intensity.



(a) (b)

Figure 5 Equatorial and meridional intensity (a) and long period (b) evolutions for the experiment performed at a Hencky strain rate of 25 s^{-1}. The vertical dashed line represents the end of elongational flow.

The time evolutions of the area underneath the $(110)_\alpha$ and the $(300)_\beta$ reflections (related to the amount of α form and β form crystals, respectively) during the experiment performed with the highest Hencky strain rate (25 s^{-1}) are shown in Figure 6. A clear increase of the area underneath the $(110)_\alpha$ reflection is observed after about 0.15 s indicating, as expected, formation of shish structures consisting of α-form crystals in line with the rheological and the SAXS observations,.

Surprisingly also an increase of the area underneath the $(300)_\beta$ peak is observed already during the elongational flow when only an increase in the SAXS equatorial intensity is observed. This could indicate formation of rod-like β-form crystals along the flow direction. During the 20 minutes of isothermal crystallization the area underneath the $(110)_\alpha$ reflection continues to increase until reaching a plateau value whereas the one related to the $(300)_\beta$ peak stays constant, indicating that the kebab are entirely made of α-form.

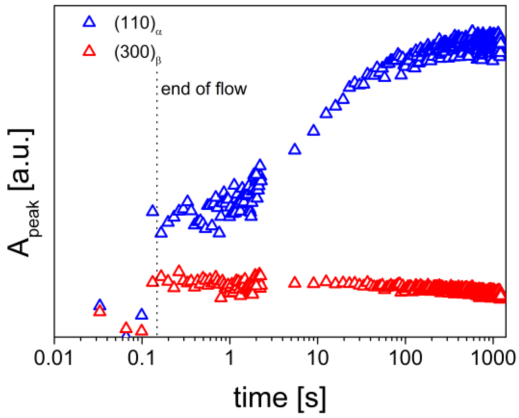


Figure 6 Time evolution of the area underneath the $(110)_\alpha$ and the $(300)_\beta$ reflections for the experiment performed with a Hencky strain of 25 s^{-1}. The vertical dashed line indicates the end of the elongational flow.

5. Are you planning follow-up experiments at DUBBLE for this project?

YES. More experiments will be performed the SER coupled with WAXD/SAXS. Since the experiments described above were performed in a period in which the beam intensity was not the highest available, we will repeat the experiments with high intensity to have a higher resolution also during the fast acquisition mode. This will permit the use of structural analysis (Ruland´s method) of shish streaks already during flow. Understanding on the shish development in length during and immediately after flow should be obtained. Possibly the experiments will be also repeated with a set of Propylene-Ethylene random copolymers, to explore the effect of chain regularity on precursors´formation.

6. Are you planning experiments at other synchrotrons in the near future?

NO.

7. Do you expect any scientific output from this experimental session (publication, patent …)

NOT YET.

8. Additional remarks