DUBBLE – EXPERIMENT REPORT

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Shifts: 6	Local contact(s): G. Portale	

1. Who took part in the experiments?

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Were you able to execute the planned experiments?

PARTIALLY. We managed to complete a series of experiment but several problems described below in the report compromised the quality of the collected data.

2. Did you encounter experimental problems?

YES. In the proposal we planned to perform the extensional rheology/X-rays experiments using a linear low density polyethylene (LLDPE) and 2 blends of LLDPE with linear low density polyethylene (LDPE). The new X-ray transparent oven mounted on an Anton Paar MCR 502 rheometer coupled with a SER (Sentmanat Extensional Rheometer) device (Figure 1) was calibrated using nitrogen flow at 5 bar present in Eindhoven laboratory whereas the nitrogen flow available at DUBBLE was only 3 bar so further calibration was needed.

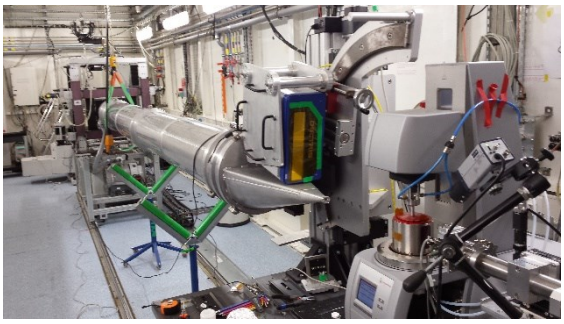

Figure 1 Experimental setup installed in the experimental hutch of DUBBLE

The planned experimental protocol was the following: the sample was initially held at 180°C for 10 mins to erase all thermal history and, subsequently cooled down to the flow temperature, T_c = 115°C. After a stabilization time at the fixed T_c a Hencky strain of 4 units at a certain Hencky strain rate was imposed to the melt. Since calibration was changed, stabilization time at DUBBLE was significantly longer than the one tested in Eindhoven. Consequently the sample started to crystallize before deformation was imposed making the experiments meaningless.

Since the setting of new experimental conditions would have taken too long and the time was limited, we decided to use a backup set of samples consisting in isotactic polypropylenes (iPP) of different molecular weight. Transient uniaxial elongational viscosities (η_{u+}) for one of the selected materials at strain rates ranging from 0.1–25 s^{-1} for the choosen T_{flow}=140 °C are given in Figure 2. The dotted lines represents the transient elongational viscosity 3η(t) for the linear viscoelastic (LVE) behavior. First, the η(t) curve was calculated based on the discrete relaxation spectrum calculated from the storage and loss moduli data at 180 °C. Then, the spectrum was shifted to the experimental temperature using the Arrhenius shift factor a_T.

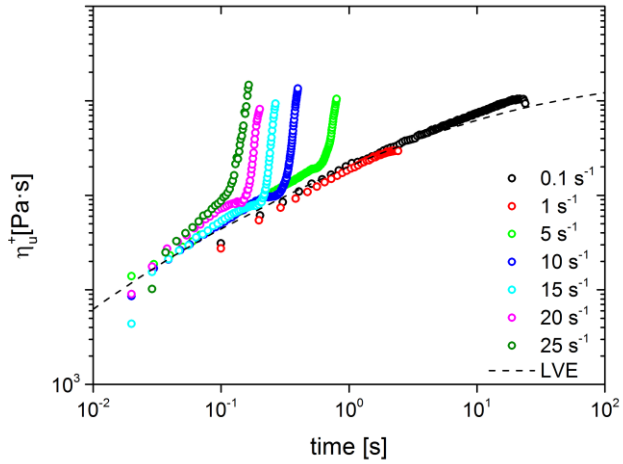

Figure 2 Tensile stress growth curves for an iPP grade over a range of Hencky strain rates measured at temperatures of 140°C (open circle).The dotted lines represents the linear viscoelastic behavior.

The deviation from LVE behavior at higher strain is clear at higher strain rates 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.

In this other set of experiments the material did not crystallize during stabilization at the experimental temperature before flow but we encountered other problems. When the maximum achievable Hencky strain of 4 was applyed to the polymer melt, one of the clamps which hold the sample to the counter rotating drums was between the two cylinders at the end of the deformation. The X-Ray primary beam was deflected and the small angle X-Ray scattering (SAXS) in the region of interest for kebab was compromised as shown in Figure 3.

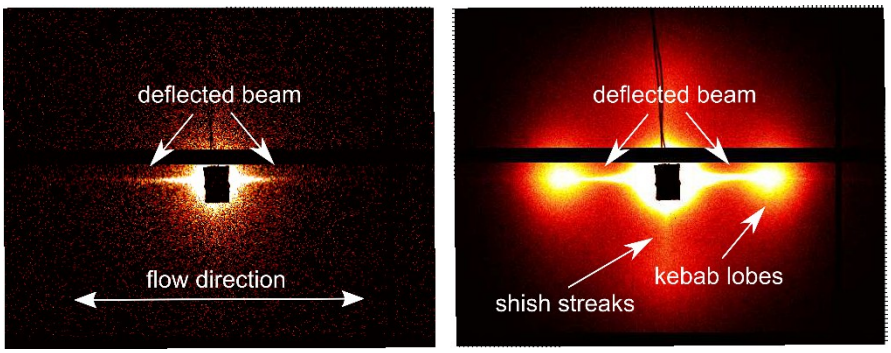

Figure 3 SAXS patterns for an iPP grade collected at the end of the deformation (left) and after 20 minutes isothermal crystallization (right). It appears clear that the deflected beam covers the intensity in the region relative to kebab (oriented lamellae) scattering.

To avoid this problem smaller deformation were used (up to 2.8), in this case the clamps were not in the region between the two drums and the beam was not deflected. Unfortunately, this deformation is just below the critical value to observe crystallization during flow, which was our main aim.

Additional problems derived from the analysis of the wide angle X-ray diffraction (WAXD) patterns. The oven used for these experiments, supplied by Anton Paar, is equipped with 4 Kapton windows with a thickness of about 250 µm each. Kapton is a polyimide developed by DuPont that remains stable across a wide range of temperatures, from −270 to +400 °C, moreover it is transparent for small angle X-ray scattering. At wide angle, it presents two diffuse halos, as typical for amorphous polymers. Since the specimen at the end of the deformation is about 200 µm, the diffracted intensity is really weak, and the signal/background ratio is consequently very small. This makes impossible to analyze the data acquired with the fast acquisition mode and the loss of frame quality was significant also in the slow acquisition mode.

Moreover, we encountered some problems with simultaneous acquisition of SAXS and WAXS patterns due to incompatibility of the macro with the recently updated ESRF server software. Experiments were programmed with short and long acquisition time, respectively. As a result of the bug the long

acquisition time patterns was obtained with the *short* acquisition time. Since the quality of the WAXS frame in fast acquisition mode was not resolved enough for properly perform the data analysis, some of the experiments needed to be repeated.

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?

NO. As already described above, our aim was that of correlate the rheology to the crystallization behaviour of the material. Unfortunately it was not possible to properly follow the structure formation during flow, so our work was limited to the isothermal crystallization after deformation, an illustrative experiment ($\dot{\varepsilon}_H$=25 s^{-1}, ε_H=2.8) is shown in Figure 4.

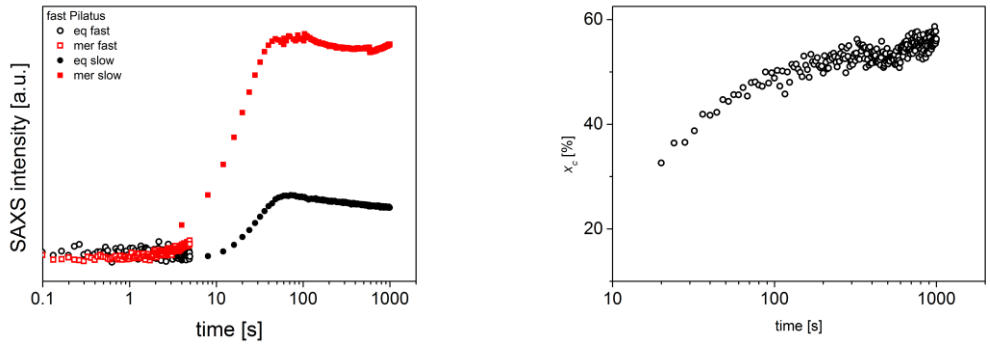

Figure 4 Left: SAXS integrated equatorial (dots) and meridional (square) intensities during isothermal crystallization after deformation. Right: Time evolution of crystallinity for one of the performed experiments.

As evident from SAXS integrated intensities and crystallinity time evolution, we were able to observe the growth kinetics of folded chain crystals (kebabs) nucleating from rod-like structures (shish) created during flow. Moreover, SAXS integrated intensity in the meridional and in the equatorial regions clearly show a different evolution. It is well known that daughters lamellae can nucleate on kebab (parents) growing from shish cores perpendicularly to flow direction. Parents lamellae give a scattering pattern in the meridional region (parallel to flow in real space) whereas daughters lamellae present two diffuse lobes in the equatorial region (perpendicular to flow in real space). The different time evolutions observed in the two regions are related to crystallization of parents and daughters: the former form immediately after flow (about 1 s) and the latter start to appear after 10 s. The

possibility to separate the two crystallization kinetics is promising for future study and upcoming experiments will be also focused on this point.

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

YES. Another beamtime is scheduled for the end of November using the same setup. The problems experienced during this beamtime helped us to recognize all the limit of the experimental setup and the needed improvements were suggested to the supplier (Anton Paar). In the *additional remarks* section a complete list of the upcoming modifications is given.

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 …)

NO.

8. Additional remarks

- We now know that the calibration of the oven has to be done with the same nitrogen flow present at ESRF. This will permit us to save precious time during next beamtime.
- We are now working without any clamps on the drums. The sample is pasted on them after a long preheating of the oven. This will permit to reach the higher deformations needed.
- Anton Paar is working on the upgrade of the old oven. Mica windows will be used instead of Kapton. Mica is completely transparent to X-rays both at small and wide angle and the quality of data will be significantly improved. Since Mica is very fragile flat windows embedded in a metal frame will be used. This will also shorten the time to mount the sample on the setup, since the old system consisted in curved sliding windows, and the preparation of an experiment was quite slow. Figure 5 shows the new configuration for the X-ray transparent oven.

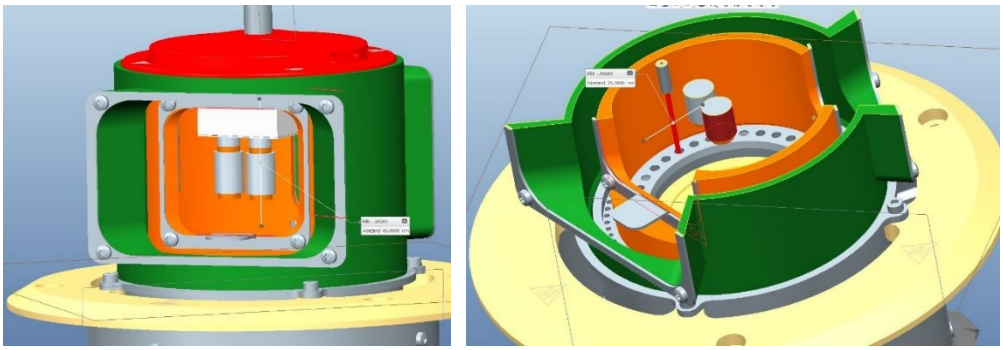

Figure 5 Schematic drawings of the new configuration of the X-ray transparent oven developed by Anton Paar.

To conclude, we are quite confident that the improvements in progress will permit us to study crystallization in processing-like conditions from the early stages (during flow) and finally to correlate this to the rheological behaviour of the material.