DUBBLE – EXPERIMENT REPORT

Beam time number: **26-02-927**		File number: 86329
Beamline: BM26-B	Date(s) of experiment: 17 February 2022 - 21 February 2022	Date of report: 29 September 2022
Shifts: 9	Local contact(s): Martin Rosenthal	

1. Who took part in the experiments?

Ruth Cardinaels[1,2], Hamid Ahmadi[2], Stan F.S.P. Looijmans[2], Paul van Heughten[2]
Affiliation:

1. Soft Matter, Rheology and Technology, Department of Chemical Engineering, KU Leuven, Belgium
2. Polymer Technology, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands.

Were you able to execute the planned experiments?

YES. We were able to perform the planned experiments.

2. Did you encounter experimental problems?

NO. The setup and the beamline instrumentation had no problems.

3. Was the local support adequate?

YES. The support of the local contact, M. Rosenthal and of the technical staff, was adequate and allowed us to efficiently run the experiments. Therefore, we lost minimal time in installing our equipment in the beamline.

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

YES. All the experimental data collected at BM26-B allowed us to study the effect of extension rate on the extensional-flow induced crystallization kinetics of LDPE, to determine the growth rate of the kebabs and to analyze the formation of twisted lamella in extensional flow.

Experimental

We performed experiments with a home-built filament stretching rheometer. This allowed us to heat a small fibril of LDPE to 150°C to erase all thermal history, and to subsequently cool it down to the crystallization temperature of 107°C, to apply a stretch with a Hencky strain between 0 and 3.2 (at strain rates between 0.1/s and 1.1/s), and meanwhile follow the crystallization, both during as well as after the stretching. Experiments were performed with the SAXS/1D-WAXS detector, as well as with the 2D-WAXS detector. Meanwhile, the rheological response was recorded with the rheometer. Apart from the initially planned experiments on LDPE, we also performed a feasibility check on measuring the crystallization in fiber-filled iPP across the complete fiber.

Results on LDPE

The analysis of the SAXS signals (Figure 1) as a function of time allowed us to extract the kebab's radial growth rate as a function of time for different values of the Hencky strain and strain rate. Thereto, we used a literature model (Keum et al. Progress Colloids Polymer Science 2005 page 114). By fitting the model on the SAXS patterns, we could extract the long period, the kebab diameter and the kebab thickness together with their size distribution (Figure 2). By doing this for the different frames taken as a function of time, the kebab growth with time could be calculated for a set of strains and strain rates (Figure 3).

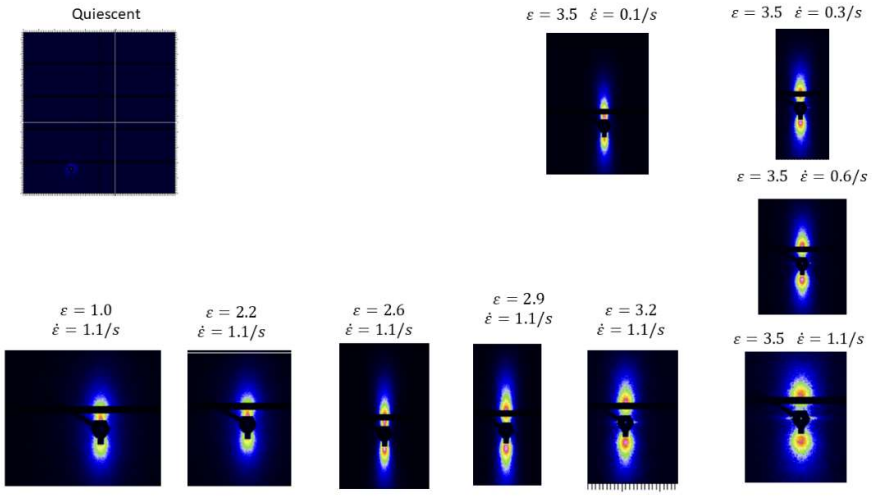

Figure 1: SAXS patterns showing the formation of shish kebabs in uniaxial extension with a sufficiently high strain and strain rate (steady state image).

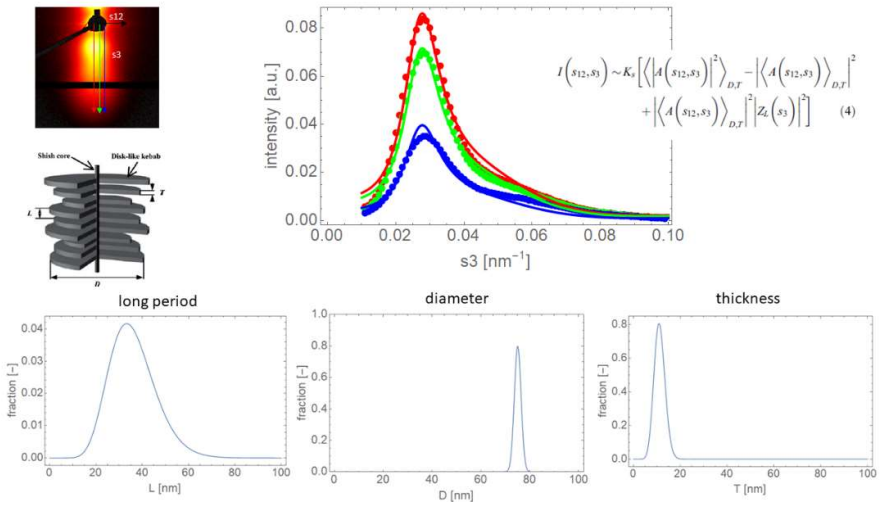

Figure 2: Representative SAXS image and schematic of the shish-kebab structure (Keum et al. 2005) with fitting of the intensity along three parallel lines with the model by Keum et al. resulting in the long period, kebab diameter and kebab thickness with their distribution.

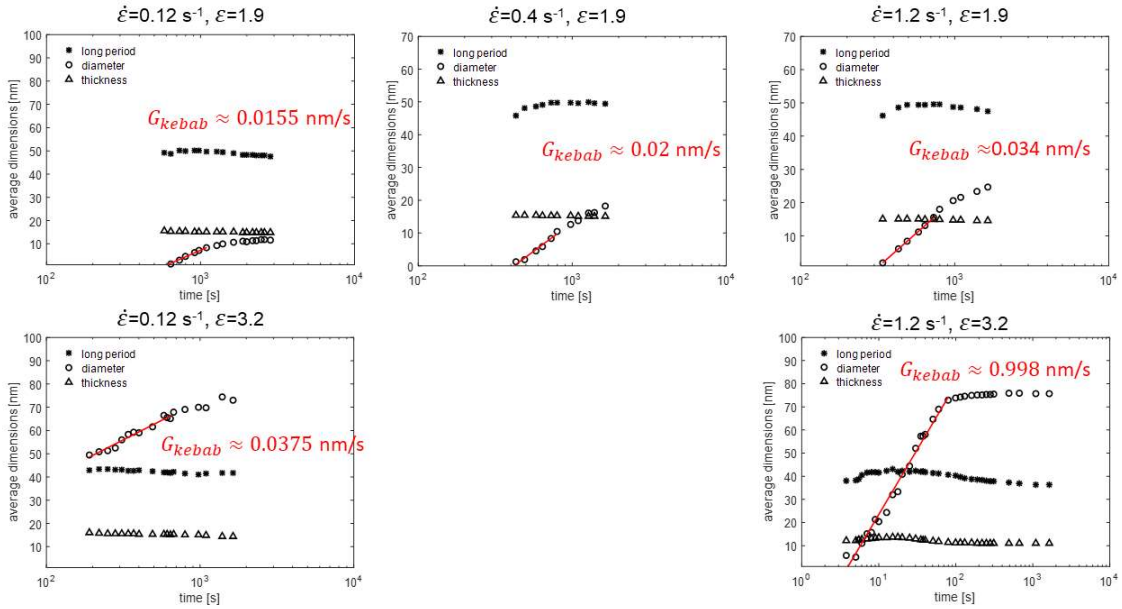

Figure 3: Results of the modelling of the SAXS data for a range of strains and strain rates, showing the kebab growth rates.

On the other hand, the 2D WAXS detector allowed us to follow the crystallinity evolution in time and the transformation of the (110) reflection from a 2-arc into a 4-arc off-axis reflection, due to lamella twisting in kebabs. Up to now, this phenomenon was mainly studied in shear flow. Our results show that the formation of twisted lamella in extension occurs already at rather low strain rates, but requires a minimum strain slightly above 1 (Figure 4).

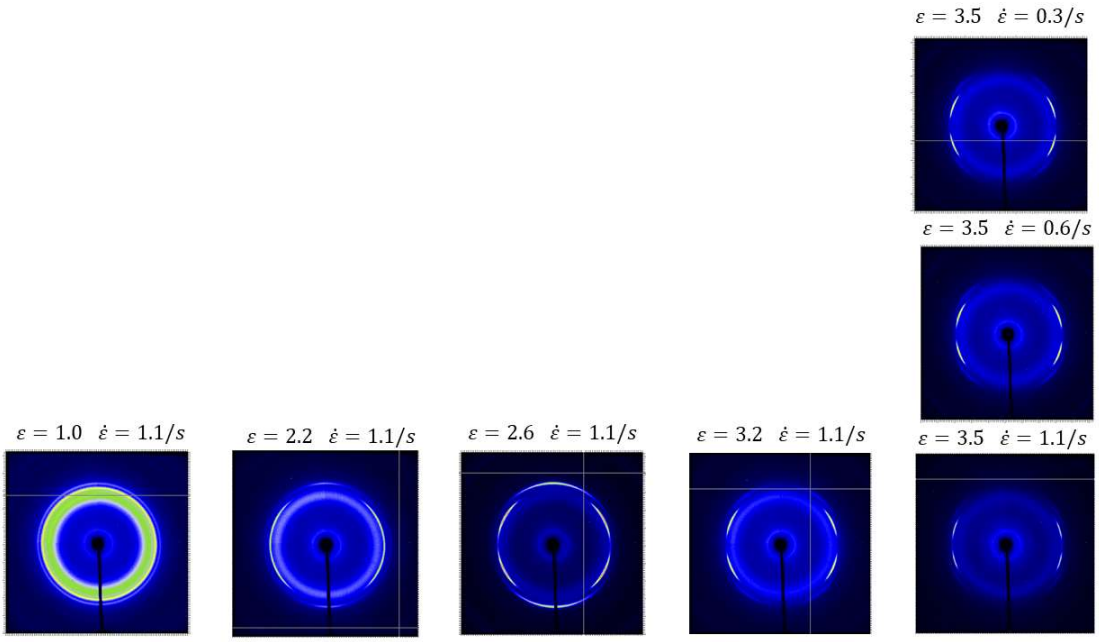

Figure 4: WAXS patterns showing the formation of twisted lamella in uniaxial extension with a sufficiently high strain and strain rate (steady state image).

Proof-of-concept tests on iPP containing a single fiber

We also performed a feasibility check on a new type of experiment with our filament stretching rheometer. This experiment was aimed at studying the effect of fibers on the extensional-flow induced crystallisation of iPP. A set of three experiments was performed on three samples namely pure iPP, iPP with the compatibilizer MAH-g-PP and iPP with a single glass fiber. After the crystallization, we scanned the complete fiber to assess the distribution of crystallinity across the fiber. The results on iPP and iPP with MAH-g-PP demonstrated the strong effect of MAH-g-PP on the crystallization kinetics of iPP (Figure 5). Interestingly, the scanning of the fiber demonstrated a significant shift from α-crystals to β-iPP crystals in particular in the neighbourhood of the fiber (Figure 5). We hypothesize that this is caused by the development of strong shear in the neighbourhood of the fiber. However, one experiment is not sufficient to unambiguously draw this conclusion.

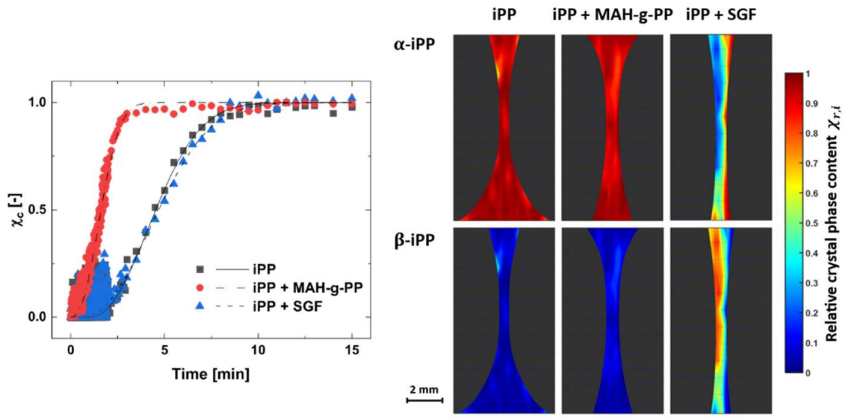

Figure 5: Relative crystallinity of the three samples on which preliminary measurements have been performed; crystallization kinetics (left) and spatial map of phase composition (right).

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

Yes. We plan experiments at DUBBLE with the same filament stretching rheometer, but for the PP-based materials for which we did a proof-of-concept check during this beamtime. The work on the LDPE is now completed and will be written out in a journal article.

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

No, not for the moment.

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

YES. The experimental data collected at BM26-B will result in scientific publications. At present we are preparing a manuscript to submit to an international peer-reviewed journal for the work on LDPE. For the work on iPP, we need to collect additional data during a next beamtime.

8. Additional remarks

DUBBLE

NWO
Netherlands Organisation for Scientific Research

DUBBLE - CLAIM FORM FOR COSTS OF TRAVEL/SUBSISTENCE

Dutch users of beam time at DUBBLE can use this form to claim full/partial reimbursement of the associated costs of travel and subsistence. The form must be returned to NWO **within 2 months of the completion of the experiment** to **dubble@nwo.nl**

Reimbursement rules (costs are reimbursed to the Main Proposer)

Travel costs
€ 400 p.p. for max. 3 persons.

Subsistence costs
Subsistence costs are reimbursed for max. 3 persons @ € 60 p.p. per day (incl. 1 day before the experiment).

Applicant (Main Proposer) : Ruth Cardinaels

Beam time number : **26-02-927**

Experiment dates : 17 February 2022 - 21 February 2022

Participants (max 3 persons):

Name : Hamid Ahmadi
Name : Ruth Cardinaels
Name : Stan F.S.P. Looijmans

Payment details

Pay to account no.: NL42RABO0158249658 (Kostenplaats Nr. 353000 Polymer Technology)

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven

Costs:

Travel costs 3 persons x 400 euro = 1200 euro

Subsistence costs 3 persons x 5 days x 60 = 900 euro

Total = 2100 euro