DUBBLE – EXPERIMENT REPORT

Beam time number: 26-02-882		File number: 81703
Beamline: BM26-B	Date(s) of experiment: 30 nov 2018 - 03 dec 2018	Date of report: 9 May 2019
Shifts: 9	Local contact(s): Daniel Hermida Merino	

1. Who took part in the experiments?

Jessica Pepe[1], Prakhtyat Hejmady[1] , Stan F.S.P. Looijmans [1], Maya Sharma[2]
Affiliation:

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

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 were correctly working.

3. Was the local support adequate?

YES. The support of the local contact, D. Hermida Merino and of the technical staff, was adequate and allow us to efficiently run the experiments.

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 are used to validate the success of the in-house developed rheometer. The outcome of the experiments is briefly described below.

Experimental

We have built a rheometer that combines (for the first time) the possibility to perform in situ x-ray characterization whilst the material undergoes a precise and locally controlled uniaxial extensional flow (Fig. 1a and 1b).

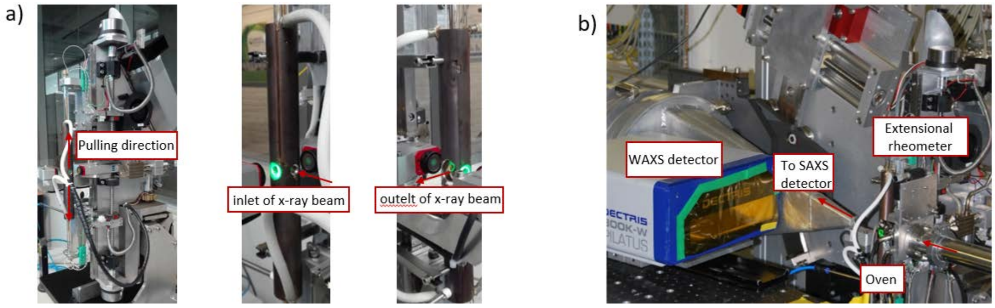

Figure 1 : a) Uniaxial extensional rheometer, b) Extensional rheometer combined with SAXS and- WAXD at ESRF

The rheometer is mounted on a motorized xyz stage that ensures perfect alignment between the midfilament point (at a fixed location) and the X-ray beam via a scan in horizontal and vertical direction (Fig. 2b and 2c) after the pre-stretch and just before starting the experiment. Based on the intensity profile at the photodiode it is possible to determine the exact centre of the sample.

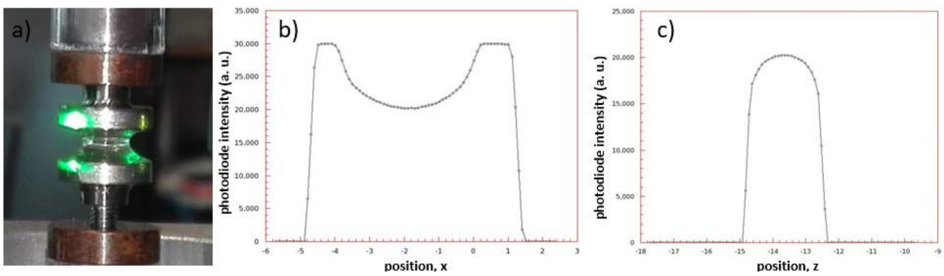

Figure 2: a) Pre-stretched sample, b) Scan in horizontal direction, c) scan in vertical direction

Extensional rheology combined with in-situ SAXS/WAXD experiments have been performed with this rheometer on a low density polyethylene sample (LDPE). The sample was placed in the oven and initially held above its melting temperature, at 150°C for 5 mins to erase all thermal history and subsequently cooled down close to the onset of crystallization. After reaching the desired temperature (107°C), and waiting for equalization of it inside the sample, a pre-stretch was applied. After complete relaxation of the polymer a Hencky strain rate was imposed to the melt for a certain time, resulting in a predefined final Hencky strain. The evolution of crystal structure and morphology was monitored during and after extensional flow, with a Pilatus 1M detector for SAXS acquisitions and a Pilatus 200K detector for 1D-WAXD acquisitions. Both SAXS and WAXD patterns, for each experiment, were collected using the following acquisition protocol: exposure time of 0.5s for an acquisition period of 60s, exposure time of 5s for an acquisition period of 60s, exposure time of 5s, with a delay between each acquisition of 25s, and for an acquisition period of 600s and exposure time of 5s, with a delay of 600s, for an acquisition period of 1080s, total acquisition time was of 30 min for each experiment. Simultaneously, the rheological response was recorded by the rheometer. The experiments were performed at a fixed flow temperature. Three different extension rates were applied and for each the effect of strain (deformation) was investigated.

Results

The SAXS pattern during flow (Fig. 3a) demonstrates the evolution of a shish kebab morphology. SAXS and WAXS patterns after cessation of flow (and complete crystallization) are shown in Fig. 3b and 3c.

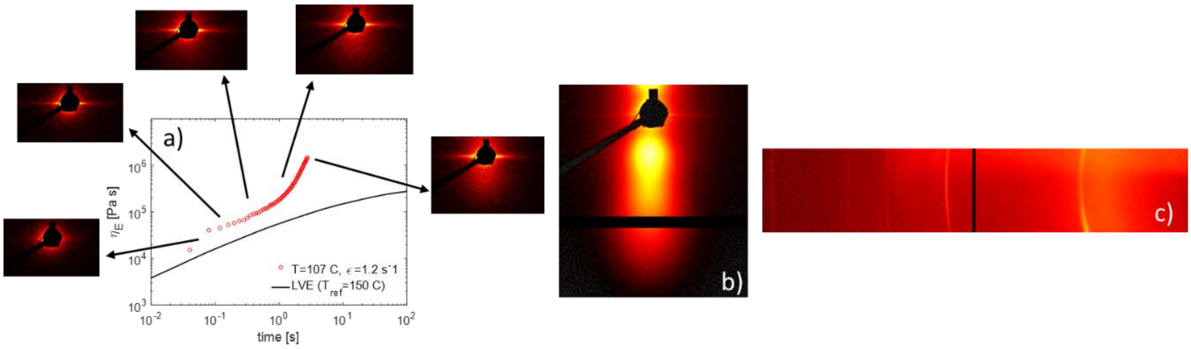

Fig. 3: a) Shish kebab morphology evolution during flow, b) SAXS pattern, c) 1D-WAXD pattern

The integrated intensities can be calculated after subtraction of the background and correction for the decrease in sample thickness. Fig. 4 shows the evolution of the meridional integrated intensity normalized with its maximum value.

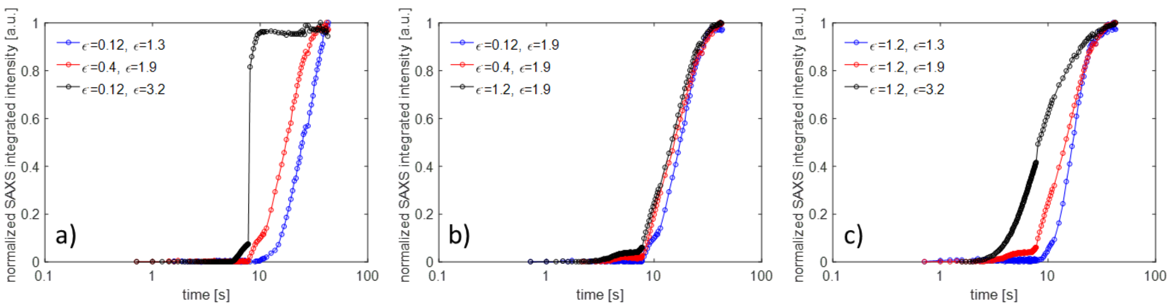

Fig. 4: Time evolution of the meridional normalized intensity: a) effect of final Hencky strain at constant strain rate of 0.12 s^{-1}, b) effect of the strain rate at a constant final Hencky strain of 1.9, c) effect of final Hencky strain at constant strain rate of 1.12 s^{-1}.

By radially integrating the SAXS pattern, in the meridional region, and after application of the Lorentz correction it is possible to evaluate the long period between the adjacent kebab stacks applying Bragg's law (Fig. 5).

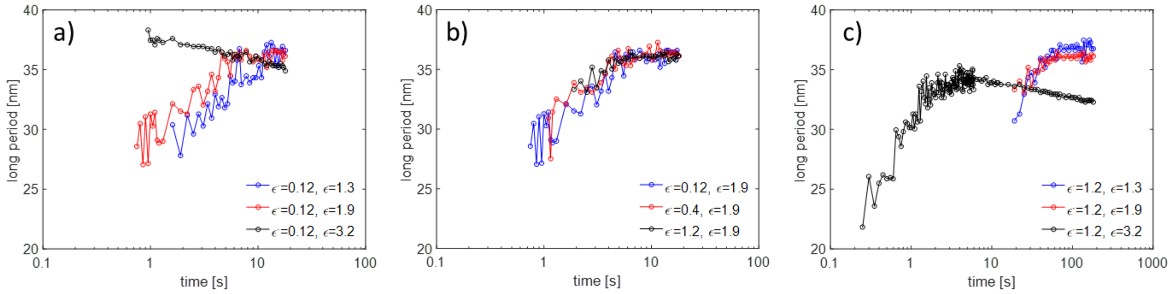

Fig. 5: Time evolution of the long period: a) effect of final Hencky strain at constant strain rate of 0.12 s^{-1}, b) effect of the strain rate at a constant final Hencky strain of 1.9, c) effect of final Hencky strain at constant strain rate of 1.12 s^{-1}.

These preliminary experiments on LDPE clearly show the feasibility of the technique and significance of the effects of extensional flow as compared to shear experiments that require higher deformation rates to achieve comparable amounts of orientation. It is evident that not only in situ X-ray experiments are possible with our in-house rheometer, but we can clearly capture the influence of deformation and deformation rate on the structure development and kinetics of crystallization.
Based on these results, this set-up can be used to create an enhanced understanding as well as modelling of extensional flow induced crystallization that is essential for the design of polymer processing operations involving extensional flow components

In addition to the experiments on LDPE, the extensional-flow induced crystallization of PVDF has been studied. For PVDF, crystallization was studied at 140°C for one constant final Hencky strain and three different strain rates. It was clear that for PVDF, much larger strain rates are required to obtain extensional-flow induced crystallization. Moreover, no shish-kebab formation was occurring.

5. Are you planning follow-up experiments at DUBBLE for this project?
NO. Because of the shutdown of the synchrotron.

6. Are you planning experiments at other synchrotrons in the near future?
YES. We have applied for beamtime in ALBA (Spain) and have received beamtime for July 2019. We will perform experiments on m-LLDPE, which is a polymer for which a full characterization of the crystallization behaviour as a function of temperature, pressure and shear has been performed in our group. Hence, these experiments will allow us to extend our models to extensional flow.

7. Do you expect any scientific output from this experimental session (publication, patent …)
YES. A publication describing our novel setup is at present in preparation for the journal Review of Scientific Instruments. For the work on PVDF, it is expected that data will result in a scientific publication after additional studies of the extensional-flow induced crystallization with our rheometer using ex-situ SAXS and WAXD characterizations are performed.

8. Additional remarks

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) : Gerrit W.M. Peters

Beam time number : 26-02-882

Experiment dates : 30 nov 2018 - 03 dec 2018

Participants (max 3 persons):

Name : Jessica Pepe

Name : Prakhyat Hejmady

Name : Stan F.S.P. Looijmans

Payment details

Pay to account no.: NL42RABO0158249658 (Project Nr. 353000/10021134)

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven