DUBBLE – EXPERIMENT REPORT

Beam time number: 26-02-790		File number: 40127
Beamline: BM26-B	Date(s) of experiment: 15 apr 2016 - 19 apr 2016	Date of report: 27 Sept 2016
Shifts: 12	Local contact(s): Daniel Hermida Merino	

1. Who took part in the experiments?

Enrico Maria Troisi[1], Harm Caelers[1] ,Rocco Di Girolamo[2]
Affiliation:

1. Material Technology Group, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands.
2. University of Naples Federico II, Napoli, Italy

Were you able to execute the planned experiments?

IN PART. As explained in detail later in this report, the performed set of experiments was incomplete

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?

NO. *Unexpectedly, we were not able to reproduce literature results, perhaps due to differences in the material properties. The outcome of the experiments is briefly described below.*

Experimental

Structural evolutios during different pressure histories were investigated by combining in-situ X-ray measurements and a pressure cell adapted on a multi-pass rheometer (MPR). This experimental setup was used in previous works as a slit flow rheometer, recent modifications allow to reach pressure up to 1000 bar and to carefully control the pressure applied on the polymer specimen. The sample (dimensions are 120 ×6 ×1.5 mm) is confined between two servo hydraulically driven pistons: pressurization and de-pressurization can be imposed by moving the pistons towards or away from each other and the set values of pressure are controlled by mean of two pressure transducer positioned near each piston. Cooling occurs by pumping a cooling medium through the cell (resulting in an average cooling rate ≈ 7°C/min) and a diamond window placed in the middle of the pressure cell allows scattering measurements (See Figure 1). Time resolved Wide Angle X-ray Diffraction WAXD) measurements were carried out with a wavelength λ =1.55 Å, using a Pilatus 300K detector (1472×195 pixels of 172μm×172 μm).

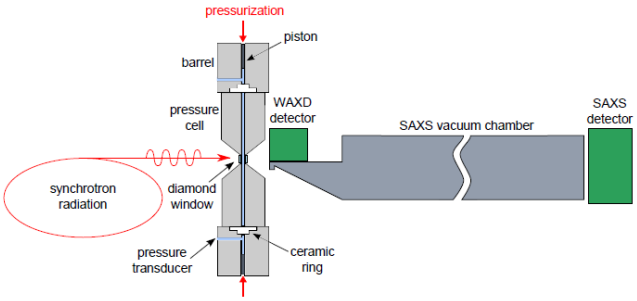

Figure 1 : Schematic drawing of the pressure cell combined with synchrotron WAXD/SAXS measurements.

The previous thermo-mechanical history was erased by keeping the sample at 170°C for 10 min before cooling to the isothermal crystallization temperature (T_c), keeping the pressure constant at 50 bar to prevent shrinkage holes formation. After temperature stabilization, the pressure was increased from 50 bar to 950 bar and kept constant during the course of the isothermal crystallizationt. The structure evolution during and after the pulse was followed by mean of combined WAXD/SAXS.

The time evolution of the relative amount of crystals in the Form I and Form II can be measured from the X-ray diffraction profiles, thanks to the diagnostic reflections (with reference to Cu-Kalpha radiation) at 9.9° for Form I and 11.9° for Form II.

Results

The final structure reached at the end of the isothermal crystallization of an highly stereoregular iPB sample at different crystallization temperatures (Tc) are reported in Figure 2. All the X-ray powder diffraction profiles have been collected at 950 bar, representing the highest pressure that the MPR could reach and control. The data of figure 2 indicate that only crystals of Form II are obtained in melt crystallization, regardless of the chosen crystallization temperature.

On the basis of previous literature results, an high amount of Form I was expected to grow directly from the melt at pressure higher than about 800 bar. The proposal was aimed at studying its formation process, however, we could not obtain the expected polymorph in the applied crystallization conditions.

The difference with respect to published result could be ascribed to differences in the molecular features of the investigated polymers (i.e. tacticity, molecular weight...).

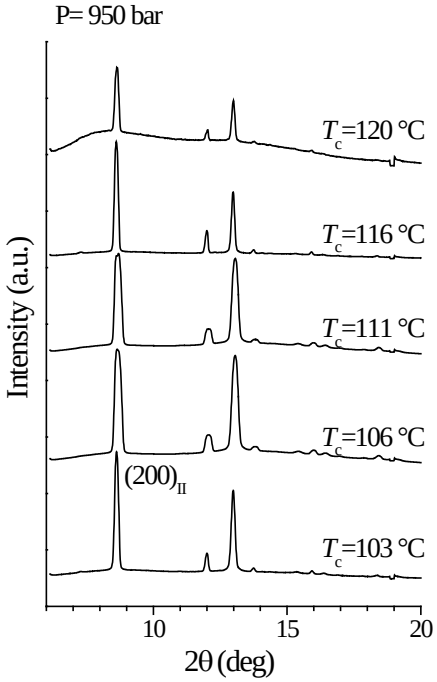

Figure 2. X-ray powder diffraction profiles of the iPB sample completely crystallized at 103, 106, 111,116, 120 °C

In a second set of experiments, the crystallization behaviour was studied in the presence of flow . Prior to each experiment, the sample was heated up to 170 °C and kept at this temperature for 10 min to erase any previous thermomechanical history. After annealing of the melt, the sample

was cooled down to the flow temperature of 115 °C where shear flow was applied using a piston speed of 10 mm/ s (displacement 15 mm) for a fixed time of 1.5 s. Prior to flow, pressure was kept constant at 50 bar to obtain an optimal filling of the slit and prevent wall slippage during flownd high pressures.

The acceleration of crystallization kinetics after flow pulses is confirmed by the on-line X-ray observation as evident from Figure 3. The iPB sample show high crystallinity immediately after the pulse (0.1 s). The sample crystallizes from the melt in Form II with a small amount of crystals of Form I. Moreover, the data of Figure 3 clearly indicate that the pressure pulse induces a rapid tranformation of Form II into Form I. This apsect is intriguing since at the chosen temperture the Form II/Form I transition should be inhibited. This prelimianry results opens the way to further experiments along this line.

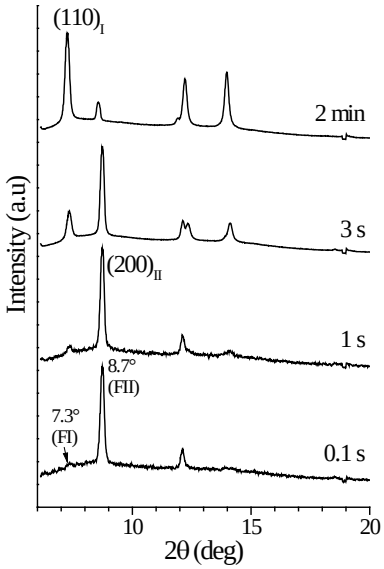

Figure 3. *Time resolved WAXD patterns of iPB sample crystalized at 115 °C after the application of a shear pulse.*

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

POSSIBLY. The experimental conditions will be firstly optimized off-line using the MPR setup and conventional dilatometers. If the formation of the sole Form I' polymorph can be achieved, repetition of the experiments at Dubble will be meaningful.

6. Are you planning experiments at other synchrotrons in the near future?
NOT AT THE MOMENT

7. Do you expect any scientific output from this experimental session (publication, patent …)
POSSIBLY. Further experimental work is required in order to understand the deviation from the expected behaviour. If this issue could be solved a scientific outcome (publication) could be expected.

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 : 26-02-790

Experiment dates : 15-19/03/2015

Participants (max 3 persons):

Name : Enrico M. Troisi

Name : Harm J. M. Caelers

Payment details

Pay to account no.: NL42RABO0158249658 (Project Nr. 353000/10018571)

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven