



## DUBBLE – EXPERIMENT REPORT

|                                |   |                              |
|--------------------------------|---|------------------------------|
| Beam time number:<br>26-02 753 |   | File number:<br>38724        |
| Beamline:<br>BM26-B            | Date(s) of experiment:<br>12/12/2016 – 16/12/2014 | Date of report:<br>04/4/2015 |
| Shifts:<br>12                  | Local contact(s):<br>Daniel Hermida Merino        |                              |

### 1. Who took part in the experiments?

Enrico Maria Troisi<sup>1</sup>, Coen Clarijs<sup>1</sup>, Harm Caelers<sup>1</sup>

Affiliation: Material Technology Group, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands.

### Were you able to execute the planned experiments?

YES. As explained in detail later in this report, a good set of experiment was performed.

### 2. Did you encounter experimental problems?

NO.

### 3. Was the local support adequate?

YES. The support of the local contact, D. Hermida Merino and the technical staff, was needed to accurately set up the experimental equipment. Both the software and the hardware worked properly and no assistance was needed after the experimental session was started.

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

YES. The most significant results will be explained in this session after a short experimental setup description:

##### Experimental

Structural and morphological evolutions 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 means of two pressure transducer positioned near each piston. Cooling occurs by pumping a cooling medium through the cell (resulting in an average cooling rate  $\approx 7^\circ\text{C}/\text{min}$ ) and a diamond window placed in the middle of the pressure cell allows scattering measurements (See Figure 1 left).

After erasing of the previous thermo-mechanical history at  $220^\circ\text{C}$  for 10 min the sample was cooled down to an isothermal crystallization temperature ( $140^\circ\text{C}$ ), keeping the pressure constant at 100 bar to prevent shrinkage holes formation. After temperature stabilization (about one minute), the pressure was increased from 100 bar to the one set for the pulse (ranging from 200 to 700 bar), kept constant for 30 s and then brought back to 100 bar. Both pressure increase and decrease were completed in less than 5 seconds. The structure evolution during and after the pulse was followed by means of combined WAXD/SAXS.

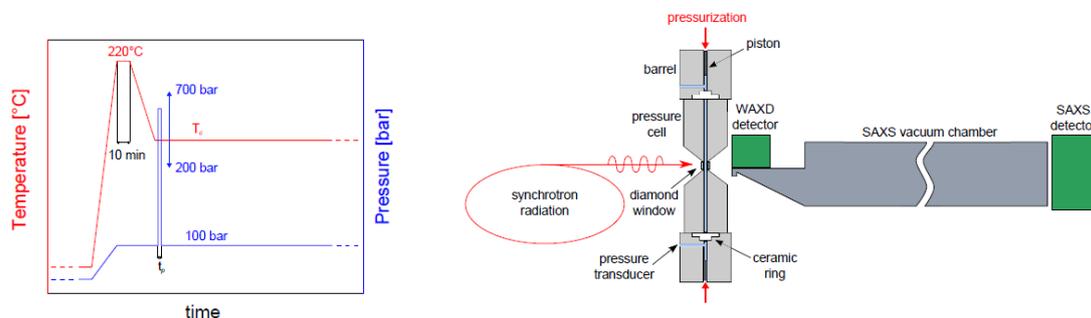


Figure 1 Left: Experimental protocol used for the pressure pulses experiments,  $t_p$  was 30 s. Right: Schematic drawing of the pressure cell combined with synchrotron WAXD/SAXS measurements.

Time resolved Small Angle X-ray Scattering and Wide Angle X-ray Diffraction (SAXS and WAXD) measurements were carried out with a wavelength  $\lambda = 1.033 \text{ \AA}$ . Acquisition of simultaneously SAXS and WAXD patterns was performed using a Pilatus 1M detector (981×1043 pixels of  $172 \mu\text{m} \times 172 \mu\text{m}$  placed at a distance of 6.47 m) and a Pilatus 300K detector (1472×195 pixels of  $172 \mu\text{m} \times 172 \mu\text{m}$  placed at a distance of 0.21 m), respectively. The detectors were triggered by an electric TTL pulse at the start of the

displacement of pistons during the pressure pulse. The structure evolution during the 30s pressure pulse was monitored using an exposure time of 5 s, the following 1200 s of isothermal and isobaric crystallization were recorded using an exposure time of 10 s and a waiting time of 20 s. The distance and tilt angle of the SAXS and WAXD detectors were calibrated using rat tail collagen and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $\alpha$ -aluminium oxide) standard powder, respectively. After correction for the background and air scattering all X-ray images were normalized for synchrotron beam fluctuations using an ionization chamber placed before the sample, and for the sample absorption using a photodiode placed on the beamstop. 2D WAXD and SAXS images were processed with the software package FIT2D to obtain 1D intensity profiles as a function of the scattering angle for WAXD ( $2\theta$ ) and of the scattering vector ( $q$ ) for SAXS. Crystallinity was calculated after deconvolution of the total intensity scattered by the crystalline ( $A_{crystal}$ ) and amorphous ( $A_{amorphous}$ ) domains:

$$X_c^{WAXD} = \frac{A_{crystal}}{A_{crystal} + A_{amorphous}} \times 100;$$

The time evolution of the relative amount of crystals in the  $\gamma$  and  $\alpha$  form was measured from the X-ray diffraction profiles, as suggested by Turner-Jones et al. [1] and Murthy et al. [2] by measuring the ratio between the intensity of the (117) <sub>$\gamma$</sub>  reflection at  $2\theta = 13.2^\circ$ , typical of the  $\gamma$  form, and the (130) <sub>$\alpha$</sub>  reflection at  $2\theta = 12.1^\circ$ , typical of the  $\alpha$  form:  $f_\gamma = I(117)_\gamma / [I(130)_\alpha + I(117)_\gamma]$  and  $f_\alpha = [I(130)_\alpha / [I(130)_\alpha + I(117)_\gamma]]$ . The intensities of (117) <sub>$\gamma$</sub>  and (130) <sub>$\alpha$</sub>  reflections were evaluated from the area underneath the corresponding diffraction peaks above the diffuse halo in the X-ray powder diffraction profiles. The long period ( $L_p$ ) was calculated from the Lorentz corrected 1D SAXS intensity profiles by simple application Braggs law:  $L_p = 2\pi/q^*$ , where  $q^*$  is the value of the scattering vector,  $q = (4\pi/\lambda)\sin\theta$ , corresponding to the maximum of the correlation peaks of the integrated intensities. The lamellar thickness ( $l_c$ ) could then be estimated as  $l_c = L_p \cdot X_{cWAXD}$ , where  $X_{cWAXD}$  is the crystallinity evaluated from WAXD.

Another measure of the structural development during the crystallization process can be evaluated using the SAXS invariant ( $Q_{SAXS}$ ) evolution defined as:

$$Q_{SAXS} = \int_{-\infty}^{+\infty} I(q)q^2 dq = 2\pi\Phi(1-\Phi)(\rho_c - \rho_a)^2$$

where  $\Phi$  is the volume fraction of the crystalline phase,  $\rho_c$  and  $\rho_a$  the density of the crystalline and of the amorphous phases, respectively.

The degree of space filling was obtained from crystallinity and invariant evolution using:

$$\xi [t] = \frac{X_c[t] - X_c^0}{X_c^\infty - X_c^0}; \quad \xi [t] = \frac{Q_{SAXS}[t] - Q_{SAXS}^0}{Q_{SAXS}^\infty - Q_{SAXS}^0};$$

where  $X_c^0$ ,  $Q_{SAXS}^0$ ,  $X_c^\infty$ ,  $Q_{SAXS}^\infty$  are the measured values of the crystallinity and of the invariant before the pressure pulse and at the end of the crystallization process.

## Results

The acceleration of crystallization kinetics after pulses of pressure is confirmed by the on-line X-ray observation as evident from the time evolution of crystallinity for experiments performed using the pressure cell combined with synchrotron radiation (Figure 2 left). The crystallization happens faster increasing the pressure applied during the pulse and, for the experiments with a pulse of 600 and 700 bar, the material starts to crystallize already during the time experienced at high pressure. The fraction of material crystallized immediately after the pulse for these two experiments is 1.5 to 3% respectively, while the final values of crystallinity is around 60% for all the experiments.

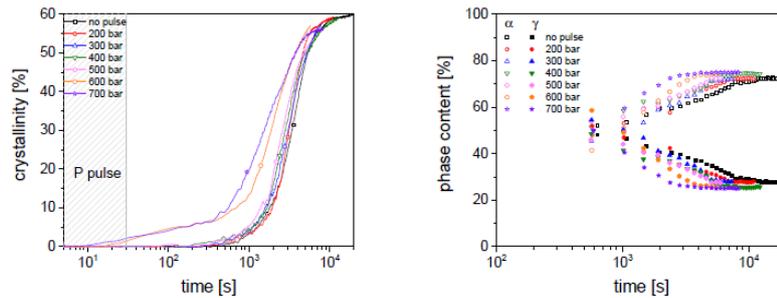


Figure 2 Time evolution of the crystallinity (left) and of the  $\alpha$  and  $\gamma$  phase contents (right) for the experiments performed coupling the pressure cell with in-situ X-ray.

Most of the crystal growth occurs upon depressurization at 100 bar, and our initial purpose to separate the nucleation from the growth process, in first approximation, still holds true.

Interestingly, the evolution of the relative amount of the two different phases formed (i.e.  $\alpha$  and  $\gamma$ ) does not seem to be affected by the pulses of pressure (Figure 2 right): in all the experiments the relative amount of  $\alpha$  - and  $\gamma$  -phase is about 50% at the beginning of the crystallization process and evolves to final values of about 70 and 30%, respectively. At these conditions of temperature and pressure (140°C and 100 bar), the growth rate of the  $\alpha$  -phase is clearly higher than the one of the  $\gamma$  -phase, in agreement with the observation of van Dronghen et al. [3] on the same material, and the final amount of  $\alpha$  -phase is prevalent. Since the amount of different phases is only dictated by the relative growth rates of the individual phases, this is an indirect evidence that the growth process is not influenced by the previous thermo-mechanical history (i.e. pressure pulses), and consequently the observed differences in the crystallization kinetics can be ascribed solely to changes in the nucleation density. In other words, extra nuclei are formed during the time experienced at high pressure, although no growth is detectable.

Further support to this hypothesis is provided by the final values of the ratios of  $\gamma$  and  $\alpha$  phases and of the lamellar thickness as a function of the pressure applied during the pulse presented in Figure 3. The ratio between the final amount of  $\gamma$  - and  $\alpha$  -phase is about 0.4 and the final value of lamellar thickness is 14 nm independently from the entity of the pressure during the pulse. Clearly, the short time experienced by the material at high pressure does not have any effect on the final

structure and morphology, these being affected only by the actual temperature and pressure at which the crystal growth happens.

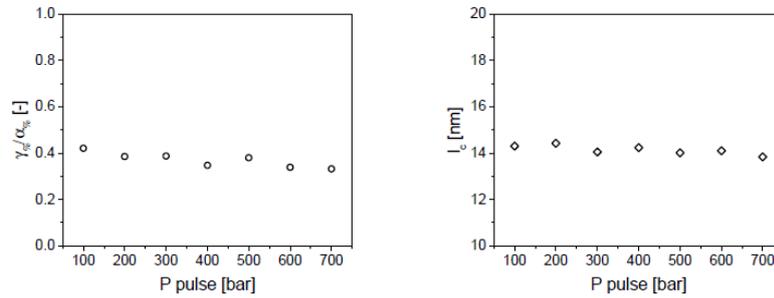


Figure 3 Final ratios of  $\gamma$ - and  $\alpha$ - phases (left) and final value of the lamellar thickness (right) as a function of the applied pressure pulse.

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

NO. These results, together with others collected in-house with a dilatometer, are sufficient for a complete paper.

**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 ...)**

YES. As stated before the results will be used for a journal paper.

**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](mailto: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 : 26-02 753

Experiment dates : 12-16/12/2015

#### **Participants** (max 3 persons):

Name : Enrico M. Troisi

Name : Coen Clarijs

Name : Harm J. M. Caelers

#### **Payment details**

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

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven