



## DUBBLE – EXPERIMENT REPORT

Beam time number: 26-02-883		File number: 91206
Beamline: BM26-B	Date(s) of experiment: 29 Oct 2018 - 02 Nov 2018	Date of report: 14 May 2019
Shifts: 9	Local contact(s): Daniel Hermida Merino	

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

Stan Looijmans<sup>1</sup>, Harm Caelers<sup>2</sup>, Susana Petisco-Ferrero<sup>1</sup>

Affiliation:

1. Polymer Technology Group, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands.
2. SABIC STC, Geleen, the Netherlands

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

NO. A diamond window of the pressure cell that was custom build for this experiment failed irrecoverably two days prior to our departure to Grenoble. At such short notice, in a weekend, we were unable to obtain a replacement window. As explained in detail later in this report, after discussing with Daniel what to do, we performed three different sets of experiments with a setup provided by the beamline.

### 2. Did you encounter experimental problems?

NO. The backup setup and the beamline instrumentation were correctly working.

### 3. Was the local support adequate?

YES. The support of the local contact, Daniel Hermida Merino and of the technical staff, was more than adequate; he helped us a lot with deciding which experiments we could perform after the setback we had a couple days prior to the beam time. Also, the last minute setup change on Sunday night led to zero measurement time being lost.

#### 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 perform the experiments that were mentioned in the proposal due to last minute irreparable failure of the equipment. Nevertheless we performed three sets of experiments which all look promising for future publication. The procedure and outcome of the experiments is briefly described below.

#### Experimental

Structural evolutions during (non-)isothermal crystallization of a large set of homo- and copolymers isotactic polypropylene were studied using the beamline's Linkam DSC device. The sample (mass approx. 5 mg) is placed in an aluminium pan of 20  $\mu$ L inside the DSC: the sample is heated above the melting temperature, kept isothermal for 2 minutes to erase thermomechanical history and subsequently cooled down to an isothermal crystallization temperature. Cooling occurs by pumping liquid nitrogen through the cell (resulting in a maximum cooling rate of 30°C/min). The experimental setup is depicted in Figure 1. Time resolved combined Wide Angle X-ray Diffraction (WAXD) and Small Angle X-ray Scattering (SAXS) measurements were carried out at a wavelength  $\lambda = 1.034 \text{ \AA}$ , using a Pilatus 300K detector (1472 x 195 pixels of 172  $\mu$ m x 172  $\mu$ m) and a Pilatus 1M detector (1043 x 981 pixels of 172  $\mu$ m x 172  $\mu$ m).

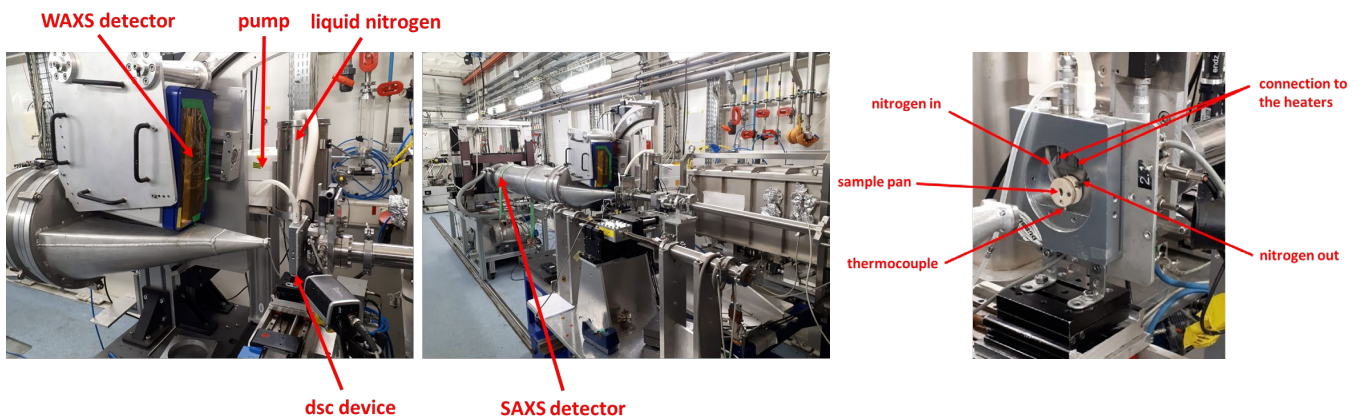


Figure 1 : Overview of the Linkam DSC stage (right) with synchrotron WAXD/SAXS setup (left).

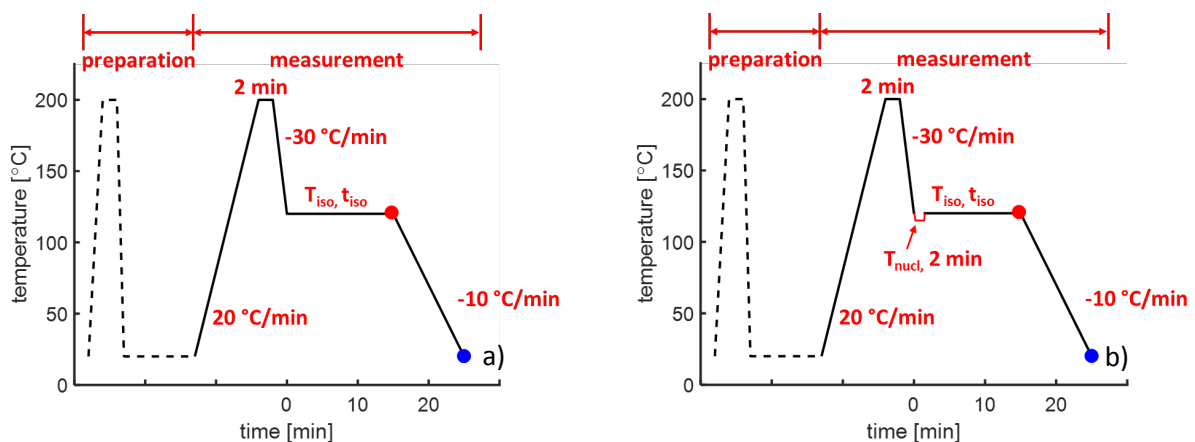


Figure 2 : Temperature protocol adopted for a) experiment set number 1 and 2, and b) experiment set 3.

## Results

In the first set of experiments, the effect of maleic anhydride (MAH) grafted polypropylene blended into several homo- and copolymers of isotactic polypropylene is studied. Previous results obtained by optical and thermal analysis show an increased crystallization rate of these blends because of a higher nucleation density as compared to both individual components. Since in these types of experiments the outcome highly depends on the quality of sample preparation, often a significant spread on the data is found. Using the combination of SAXS and WAXD measurements we were able to quantify the crystallization kinetics of a representative material volume of samples with a different MAH content, and confirm the faster crystallization of the blends compared to its individual components, particularly at higher crystallization temperatures. In Figure 3 an example is given where for three different temperatures the volumetric crystallinity is plotted as function of time for various weight fractions of malinated polypropylene, where it can be seen that the neat i-PP and MA-PP crystallize slower than their 2.5 wt% and 5 wt% blends. Similar results were obtained for different molecular weights and comonomer fractions.

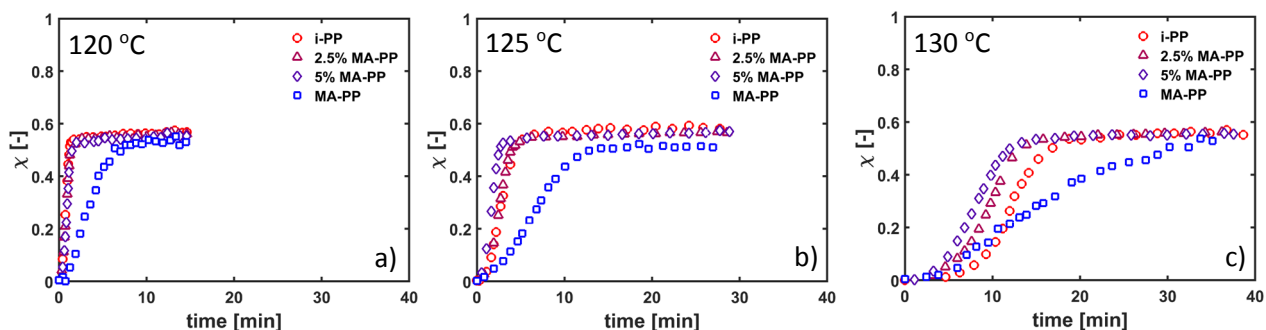


Figure 3 : Volumetric crystallinity of the various samples isothermally crystallized at a) 120 °C, b) 125 °C and c) 130 °C.

In this first set of experiments, a discrepancy with respect to literature data on i-PP was observed; the second main reflection of the  $\alpha$ -phase i-PP crystal, corresponding to the 040 crystallographic distance, seems to be a superposition of two reflections, that have approximately the same shape and height and become only visible when crystallizing at high isothermal temperatures. At first, we thought that this different distance was related to the maleic anhydride group, giving rise to a larger inter-planer distance because of its large volume with respect to the hydrogen it replaces on the i-PP chain. This hypothesis however, was countered by observing the same behaviour in the neat i-PP sample at various temperatures.

This led to a second set of experiments, in which we tested under the same conditions, i.e. crystallization temperatures and acquisition times, neat homo- and copolymers of various molecular weights. At this point we finished the data analysis of all the samples, and consulted an expert in the field (prof. Bernard Lotz, CNRS) to help us with the data interpretation. We believe that this phenomenon combination of a highly brilliant light source, in combination with relatively long acquisition times (leading to little noise) made this superposition visible. In Figure 4 the region of interest of the diffraction patterns is shown over time, where the samples are cooled from the melt to the indicated isothermal temperature. Upon subsequent cooling, the shift with temperature is not the same for both reflections, leading to merging of the two peaks at lower isothermal temperatures (or when crystallized under a temperature gradient), while when crystallized at higher temperatures, at room temperature still the distinct reflections are visible. When a homo-polymer is compared to a random copolymer of similar molecular weight, the second peak is less visible, and appears as a shoulder on the strongest (040) $_{\alpha}$  reflection, as is shown in Figure 5. It should be noted that in all these samples the amount of  $\gamma$ -phase is negligible compared to the  $\alpha$ -phase, and hence the total intensity of the second peak cannot be related to the orthorhombic phase.

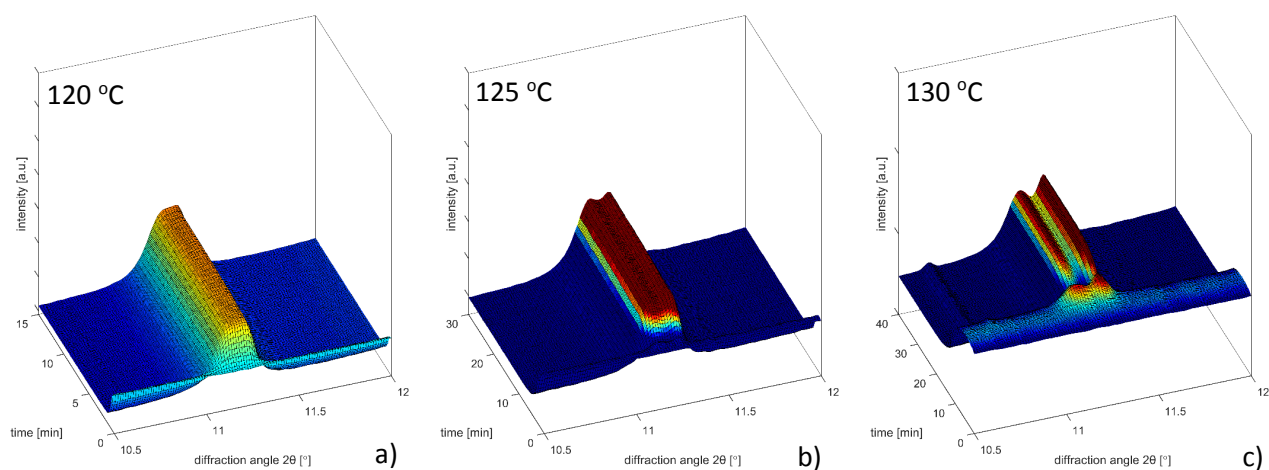


Figure 4 : Region around the  $(040)_\alpha$  reflection of neat *i*-PP isothermally crystallized at a) 120 °C, b) 125 °C and c) 130 °C.

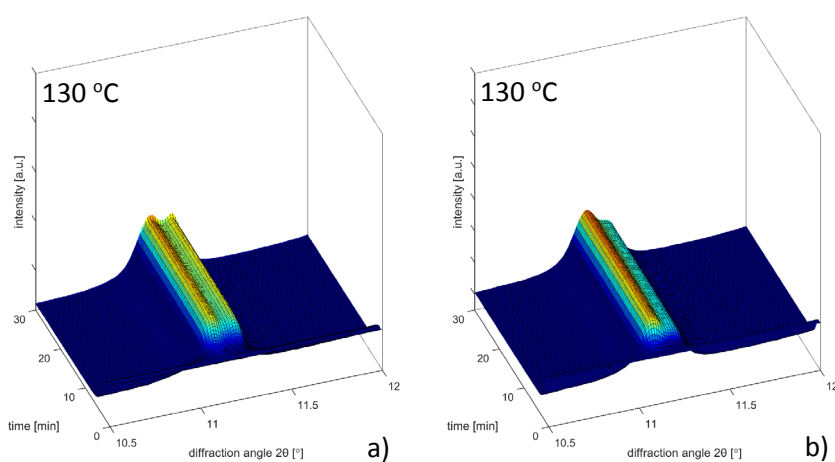


Figure 5 : Region around the  $(040)_\alpha$  reflection of a) a neat *i*-PP homopolymer and b) a random copolymer, isothermally crystallized at 130 °C.

In the third set of experiments a random copolymer was isothermally crystallized at various isothermal temperatures ranging from 114 °C to 126 °C. In this case, both the thermal history as depicted in Figure 2a, as well as Figure 2b was applied to the sample, in order to capture the difference in nucleation density and observe a faster crystallization kinetic. These experiments will be used in future work; we aim to extend the method of De Santis and Pantani, where all model parameters of single phase crystallization model can be obtained from simple (F-)DSC measurements, to be applicable in a multiphase system, e.g. a commonly observed mix of  $\alpha$ -phase and  $\gamma$ -phase *i*-PP. In order to do so, reference data on the exact amounts of the individual crystal phases was collected during this experimental time, see Figure 6. We were able to execute experiments over a range of temperatures, and to observe a change in preferred crystallographic structure from alpha to gamma with increasing temperature. Moreover, this experimental dataset forms the crucial input for the ongoing work on the extension of the aforementioned method.

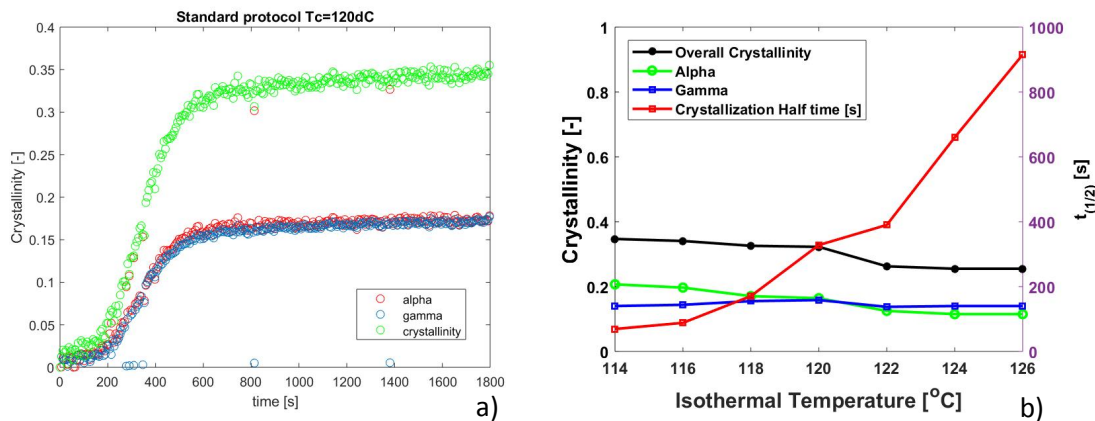


Figure 6 : a) Typical example of crystallinity development and the deconvoluted mass fractions of alpha and gamma phase as a function of time at 130 °C. b) The final crystallinities, relative alpha and gamma content, and the crystallization half time as a function of the isothermal crystallization temperature.

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

UNFORTUNATELY NOT. We have in mind several interesting experiments using this equipment for in-situ x-ray measurements. However, because of the shutdown of the synchrotron and DUBBLE beamline we are forced to do perform these measurements elsewhere.

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

YES. We applied for beam time at the DESY synchrotron in Hamburg for the execution of the initially planned experiments using the pressure cell.

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

YES. With the data obtained we see interesting features in the crystal structure of polypropylene. Further work is required in order to understand the origin of this unexpected behaviour. Once this issue is solved a scientific outcome (publication) is expected. Besides that, the data forms a valuable basis for extension of our crystallization model, which may also lead to a scientific publication.

### 8. Additional remarks

NONE.



## 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).

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**Applicant (Main Proposer)** : Gerrit W.M. Peters

Beam time number : 26-02-883

Experiment dates : 29/10/2018 – 02/11/2018

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

Name : Stan F.S.P. Looijmans

Name : Susana Petisco-Ferrero

#### **Payment details**

Pay to account no.: NL42RABO0158249658 (Project Nr. 353000/10024984)

Name: TECHNISCHE UNIVERSITEIT EINDHOVEN

City: Eindhoven