DUBBLE – EXPERIMENT REPORT

Beam time number: 26-02-964		File number: 94876
Beamline: BM26	Date(s) of experiment: 15 June 2023 - 19 June 2023	Date of report: 15 September 2023
Shifts: 12	Local contact(s): Martin Rosenthal	

1. Who took part in the experiments?

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

[1]Processing and Performance of Materials, Department of Mechanical Engineering, Eindhoven University of Technology, the Netherlands

[2]Soft Matter Rheology and Technology, Department of Chemical Engineering, KU Leuven, Belgium

2. Were you able to execute the planned experiments?

YES. We were able to perform the planned experiments.

3. Did you encounter experimental problems?

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

4. 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.

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

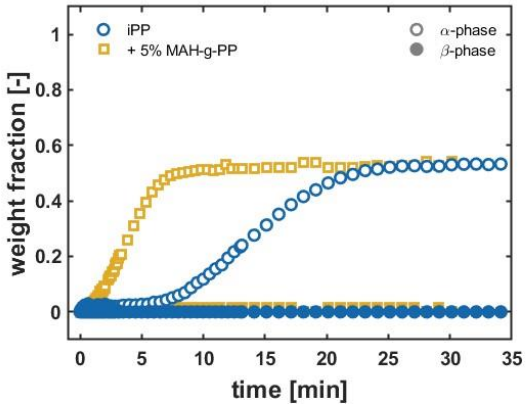
YES. We could collect a comprehensive dataset at BM26. The outcome of the experiments is briefly described below.

Experimental method

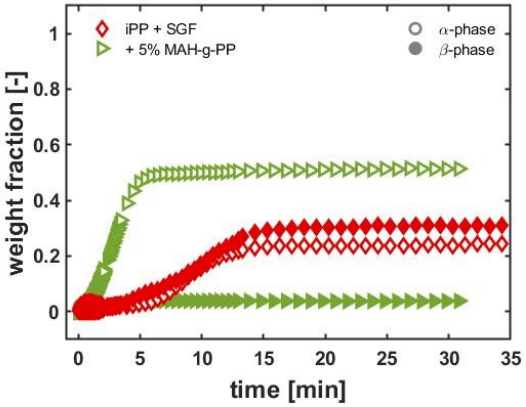
The experimental setup used is an in-house built filament stretching extensional rheometer (FiSER). The design of the FiSER concurrently allows for measuring the rheological response and performing in-situ X-ray experiments during elongation since the center of the filament remains at a constant position while stretching. A constant strain rate is applied by means of a control scheme for the speed of the bottom and top pistons, which simultaneously move apart. The two plates of the FiSER are heated up to 210 °C before the sample is placed. The polymer disk is then placed and heated up to erase its thermomechanical history. Consecutively, the sample is compressed to obtain proper contact with both plates and to attain a cylindrical shape, whereafter the sample is pre-stretched to create a concave shape. Firstly, the sample is cooled down at a rate of 5 °C/min, which is the maximum cooling rate of the device, to the desired temperature. In the center of the filament, a uniaxial elongational flow is applied at a constant strain rate of 1 s^{-1} until a true strain of 3 is reached. The midfilament diameter, which is the smallest diameter in the concave shape, is measured using a laser micrometer, and is controlled during the experiment to attain a constant Hencky strain rate. Throughout the experiment, the temperature is held constant, and pre-heated nitrogen gas is flushed to ensure a homogeneous temperature of the entire sample and to prevent oxidative degradation of the matrix material.
The collected data is analyzed using the software program Fit2D, developed by the ESRF. A mask is applied to the data to exclude the pixel regions of the beam stop and gaps in the detector. Combined with the X-ray experiments, the extensional rheology of the samples is measured using the FiSER. However, due to a too low force, no reliable rheological data could be obtained. This however, can still be improved by performing measurements using a different load cell.

Crystallization kinetics

Clearly, as shown in Figure 1, the neat iPP, disregarding the fiber, starts crystallizing after the flow has been applied. The MAH-g-PP causes an acceleration in kinetics. A glass fiber in a neat iPP matrix introduces the development of β-phase crystals as opposed to the compatibilized matrix with a glass fiber. β-phase crystals form for neat iPP with fiber, because of the alignment of α-phase nuclei. The formation of β-phase nuclei, as suggested by Varga, is an explanation for the distinct development of β-phase from the bulk. A fiber disturbs the applied elongational flow in the midfilament center, hence allowing the polymer chains to rotate, orient, and stretch, aligning into α-phase nuclei. Yet, the formation of aligned α-phase nuclei is a necessary, but not sufficient condition for the nucleation of β-phase. In the case of neat iPP, the elongational flow is not able to orient the polymer melt and hence, the formation of β-phase is prohibited.



(a)



(b)

Figure 1 Weight fraction evolution measured via in-situ WAXD during isothermal elongation at a constant strain rate of 1s^{-1} to a true strain of 3, and subsequent isothermal crystallization at a temperature of 133 °C. The presented samples are (a) iPP, and iPP with 5% MAH-g-PP, and (b) iPP with a single glass fiber, and iPP with 5% MAH-g-PP and a single glass fiber.

Crystal types and orientation

The structural and morphological differences in the midfilament point between iPP, iPP with 5% MAH-g-PP, iPP with an SGF, and iPP with 5% MAH-g-PP and an SGF can best be understood by considering the WAXD and 2D-SAXS patterns, as presented in Figure 2. The isotropic microstructure of the neat iPP indicated that the polymer chains have had sufficient time to relax before the onset of crystallization so that no oriented shish-kebab structures are formed. Hence, the lack of β-phase crystals can be explained similarly, as no oriented α-phase layer is present. The apparent shish, shown in the 2D-SAXS figure, are derived from the scattering of the filament edges, as the diameter of the filament approaches the horizontal size of the X-ray beam.

Adding the compatibilizer to the neat iPP matrix gives rise to an oriented crystal morphology perpendicular to the flow direction. This is in contrast to shear flow, where compatibilization leads to a decrease in orientation at the lamellar level. Consequently, the developed orientation can be attributed to the early onset of crystallization, occurring during the elongation of the filament. The formation of β-phase polypropylene is believed to be hampered by the abundant nucleation density, causing the available space to be rapidly filled.

In the case of a single glass fiber (SGF), the slight orientation is not apparent due to the sagging of the fiber with respect to the measurement position. Although the formation of β-phase has not been influenced by the downward shift, orientation of the β-phase cannot clearly be observed. Here, the addition of the compatibilizer results in the highest observable orientation perpendicular to the flow direction on the lamellar level. A negligible amount of oriented β-phase is observed, which is considered to be present towards the edges of the filament, where a slight shear component may be present.

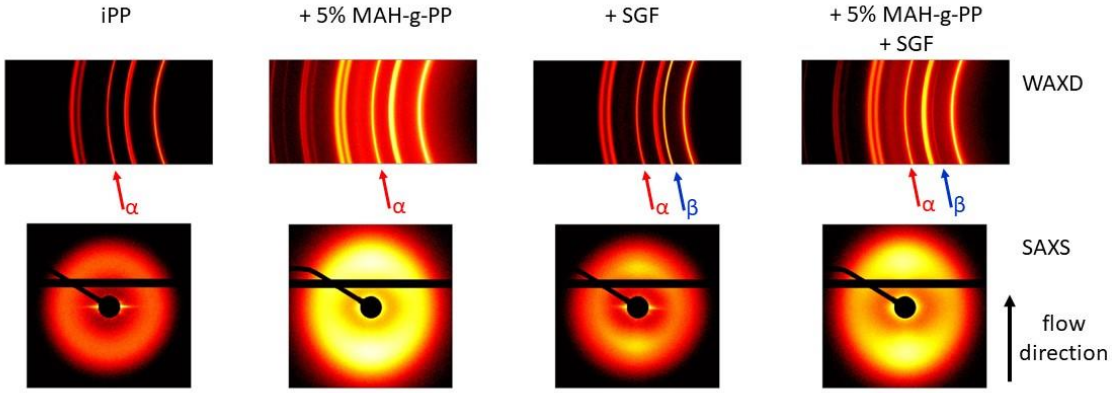


Figure 2 The final frame, where crystallization has finished, of the in-situ WAXD (top) and SAXS (bottom) patterns. The samples from left to right are iPP, iPP with 5% MAH-g-PP, iPP with a single glass fiber, and iPP with 5% MAH-g-PP and a single glass fiber. The filaments are stretched to a true strain of 3 at a strain rate of 1 s^{-1} at a temperature of 133 °C. The measurement is performed at the midfilament point.

The relative phase content of the four different samples under consideration is compared in Figure 3. Here, a two-dimensional X-ray scan in the combined SAXS/WAXD setup has been performed over the

fully crystallized filaments, i.e., after the previously described elongation is finished. Visualization of the filament is done by measuring the diameter using the laser micrometer over the length of the filament, assuming cylindrical symmetry around the central axis of the filament. For the neat iPP, iPP with 5% MAH-g-PP, and iPP with 5% MAH-g-PP and a single glass fiber, α-phase is clearly the dominant polymorph. The formation of small amounts of β-phase is present mainly towards the edges or distant from the midfilament point. The introduction of a single glass fiber in the neat iPP matrix has a substantial effect on the crystal formation in the bulk over the entire volume of the filament. This is a peculiar observation, as the volume fraction of the fiber is calculated to be as little as 0.00045%.

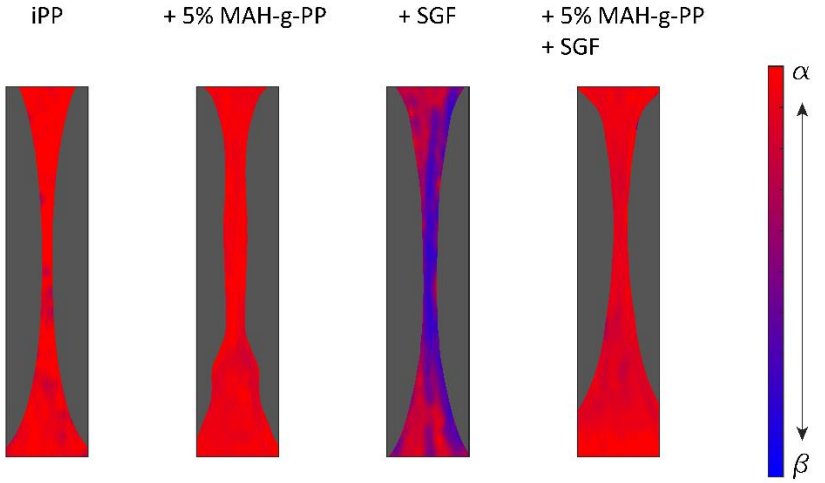


Figure 3 Visualization of two-dimensional scan where the relative α- and β-phase content is presented after stretching and complete crystallization. The samples from left to right are iPP, iPP with 5% MAH-g-PP, iPP with a single glass fiber, and iPP with 5% MAH-g-PP and a single glass fiber. The filaments are stretched to a true strain of 3 at a strain rate of 1 s^{-1} at a temperature of 133 °C. The ex-situ scan is performed at am temperature of 20 °C. In the stretching direction, line scans are made every 0.5 mm, containing 42 points each equally distributed over a width of 4 mm.

<u>iPP with rubber particles</u>

A set of experiments could be performed to study the crystallization kinetics of iPP with and without rubber particles at various temperatures. These data still need to be processed.

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

YES. To complete the part of the work on the effect of rubber particles on the extensional-flow induced crystallization.

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

NO.

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

YES. A publication has been drafted on the effect of one fiber on the extensional flow induced crystallisation. The results obtained on the rubber-filled PP will also be incorporated in a publication, but will need additional experiments before it can be completed.

9. Additional remarks

No extra remarks.

DUBBLE - CLAIM FORM FOR COSTS OF TRAVEL/SUBSISTENCE

Applicant (Main Proposer) : Ruth Cardinaels

Beam time number : 26-02-964

Experiment dates : 15 June 2023 – 19 June 2023

Participants (max 3 persons):

Name : Ruth Cardinaels

Name : Hamid Ahmadi

Name : Stan F.S.P. Looijmans

Payment details

guesthouse Ruth Cardinaels	208.45
Gas after trip	119.68
Gas before travelling back	121.74
payage going	50.3
payage coming back	50.3
food 15 june Ruth Cardinaels	9.39
food 16 june Ruth Cardinaels	17.8
food 17 june Ruth Cardinaels	19.04
food 18 june Ruth Cardinaels	16.72
car rental	856.51
som	1469.93