EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

	Experiment title: Oxalamide based organic compounds in polymer melts: How are self-assembly, shear enhanced crystallization and viscosity suppression related?	**Experiment number**: 26-02-874
Beamline: BM26B	**Date of experiment**: from: 18-07-2018 to: 24-07-2018	**Date of report**: 21-08-2018
Shifts: 15	**Local contact(s)**: Daniel Hermida Merino	*Received at ESRF:*

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Report: In the allocated beamtime, we have tested the effect of various oxalamide based nucleating agents on the shear beahvior of of *i*PP (Figure 1). For this report we particularly focus on nucleating agent OXA3,6 as this exihibited excellent viscosity suppression in previous work which could not be explained using molecular modelling (Figure 2, left). Due to the lowered viscosity, applying a shear pulse to *i*PP with OXA3,6 as nucleating agent resulted in a suppressed shear behavior and the formation of thinner shear layers (Figure 2, right). From the information in Figure 2, we were unable to identify whether or not shear enhanced shish-formation occurs in iPP containing OXA3,6, as the viscosity suppression dominated the shear response. Therefore, the question that we wanted to answer in this work: Do OXA3,6 particles induce shear enhanced shish formation, despite the fact that they lower the viscosity?

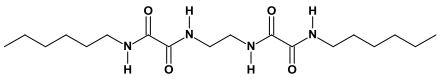
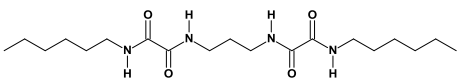
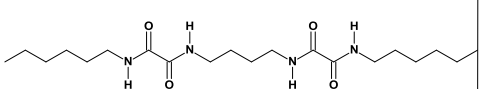
Nucleating agent		T_m (°C)
OXA 2,6		287
OXA 3,6		231
OXA 4,6		247

Figure 1. Chemical compositions of the three nucleating agents tested in this study.

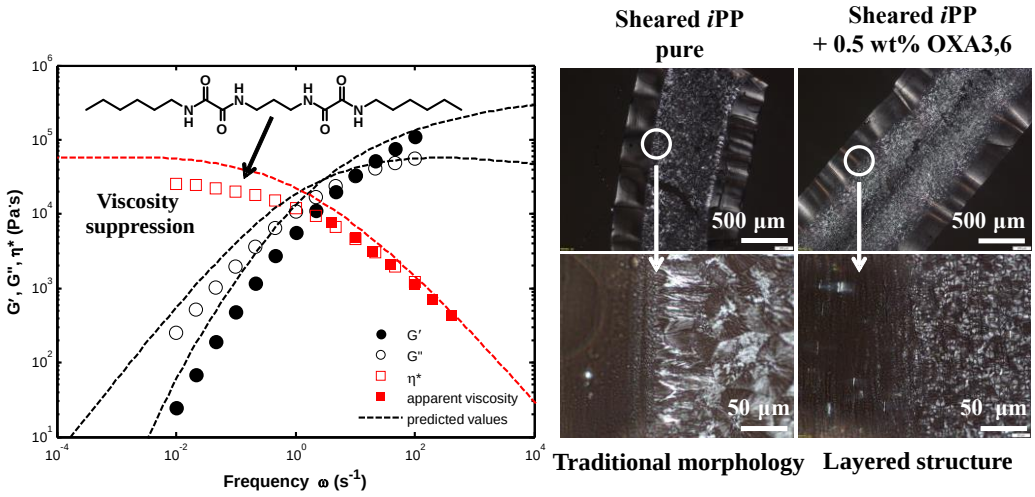


Figure 2. Left) Viscosity suppression compared to predicted values obtained from molecular modelling (dotted lines), right) Decrease in shear layer thickness in the presence of OXA3,6 after shear induced crystallization due to suppressed viscosity, while the crystallite size decreases indicating that crystallization is enhanced.

The materials were loaded in a multi-pass rheometer, where well defined shear pulses were applied, after which the SAXS spectra during and after the shear were collected. These pulse experiments were performed at temperatures of 150 °C (to facilitate shear-induced crystallization) or 160 °C (to facilitate shear enhanced shish-formation, without getting exessive crystalliation). Furhtermore, the materials were molten at higher temperatures to evaluate how long it takes to fully melt the shear-induced precursors/shishes (up to 220 °C).

Figure 3 depicts the SAXS and WAXD patterns obtained after performing 10 consecutive shear pulses with a one minute interval on the *i*PP samples. Through the application of such a protocol, we subject the polymer melt to a shear pulse (100 mm/s, 15 mm) and allow the material to relax only for one minute. When the effect of shear on the melt is unable to relax in one minute time-frame, the application of the additional pulse builds on the shear induced morphology, thereby slowly generating a shear induced morphology. As can be seen from Figure 3, it requires 5 shear pulses to generate shishes for pure the iPP sample (inducated by the horizontal streak in scattering intensity). In contrast, for the sample having 1.0 wt% OXA3,6, a streak in horizontal scattering intensity is already observed in the first pulse, which becomes more dominant with every consecutive pulse. The sample containing 0.5 wt% OXA3,6 behaves similar, although the shish formation becomes evident only after 3 shear pulses. Similarly, oriented kebab growth occurs also during this shear protocol (evident after the 10^{th} shear pulse in both WAXD and SAXS), which increases in intensity as the OXA3,6 concentration increases.

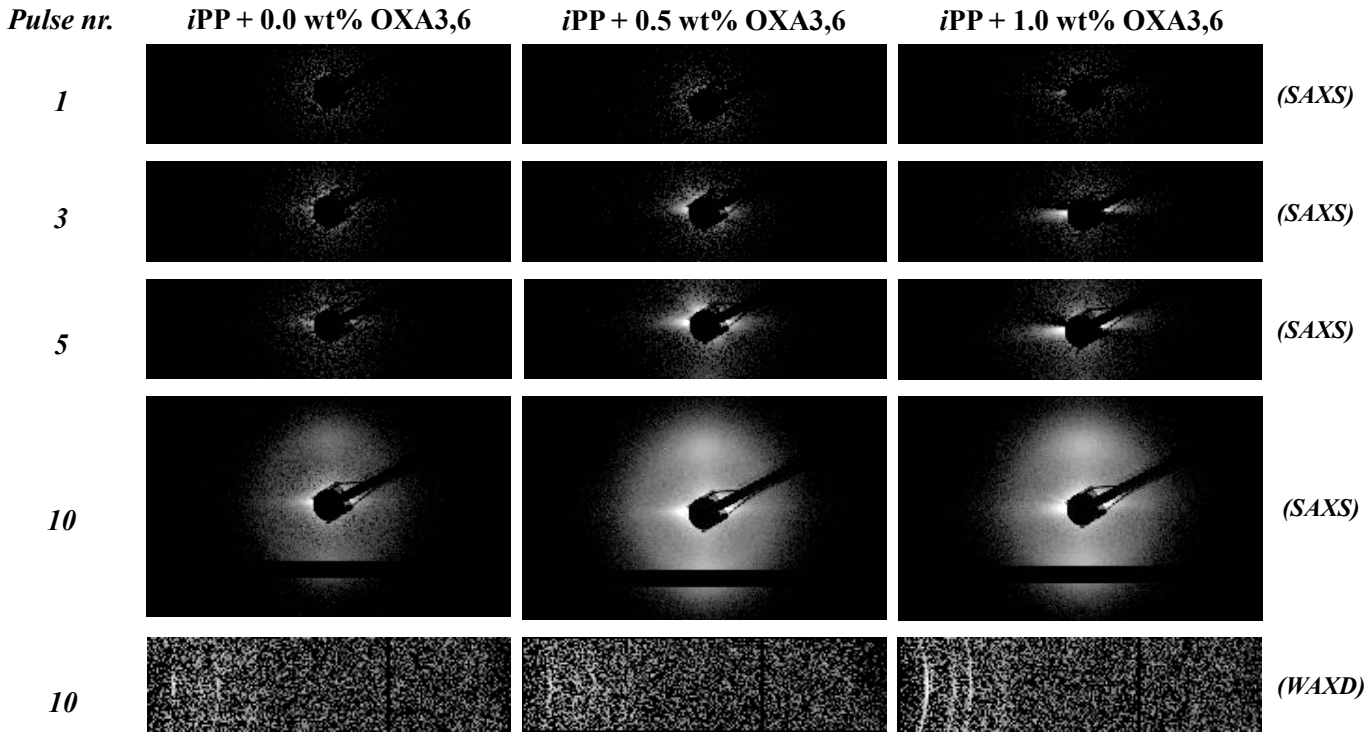


Figure 3. 2D-SAXS pattern obtained directly after the application of 10 consecutive shear pulses (100 mm/s, 15 mm, 160 °C), performed at 1 minute intervals.

Similarly, the polymer response upon application of these consecutive shear-pulses was monitored using the multipass rheometer (Figures 4-6), where we observe the the samples having 0.5 wt% OXA3,6 indeed exhibit a more dominant pressure build-up compared to the *i*PP samples.

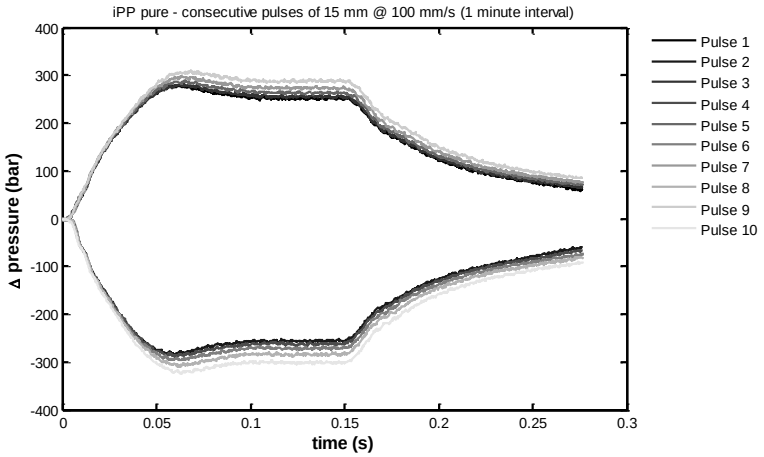


Figure 4. Pressure build-up observed during the consecutive MPR pulses performed on pure *i*PP (odd pulses are downwards, resulting in a positive pressure build-up, whereas the even pulses are upwards, resulting in a negative pressure build-up. The pulses were applied at 100 mm/s for 15 mm at 160 °C with 1 minute intervals.

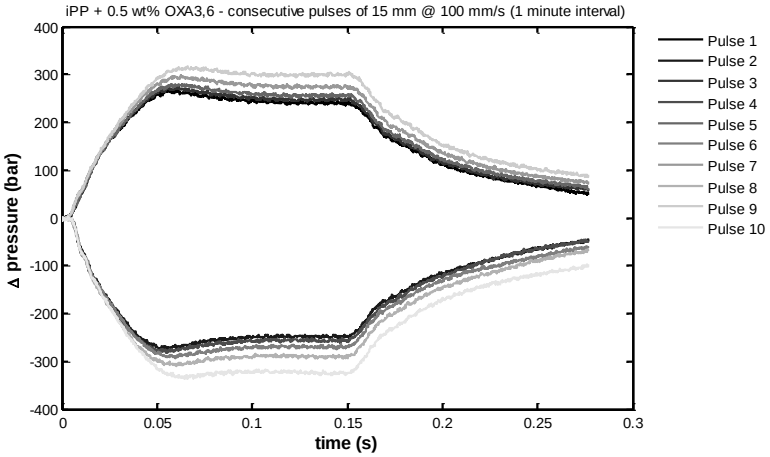


Figure 5. Pressure build-up observed during the consecutive MPR pulses performed on *i*PP containing 0.5 wt% OXA3,6, following the same protocol as shown in Figure 4.

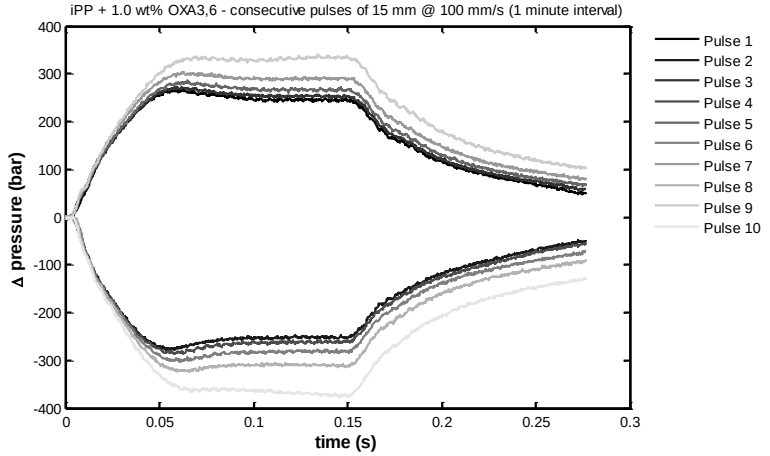


Figure 6. Pressure build-up observed during the consecutive MPR pulses performed on *i*PP containing 1.0 wt% OXA3,6, following the same protocol as shown in Figure 4.

For the data shown in Figures 4-6, the plateau value during steady shear is an indication for the complex viscosity of these materials. When we plot the plateau pressures and normalize this to the plateau pressures of the first two iPP pulses (both the backward and forward pulses, Figure 7) we can confirm the following behavior: 1) The samples containing OXA3,6 initially exhibit a lowered apparent viscosity compared to the pure *i*PP, and 2) With increasing OXA3,6 content, the apparent viscosity increases faster than pure *i*PP during consecutive pulses, indicating that OXA3,6 stimultes shear enhanced shish formation and thereby generating a larger shear layer. Lastly, leaving the materials to crystallize under isothermal conditions after application of the shear protocol results in rapid kebab growth (Figure 8, for sample having 1.0 wt% OXA3,6). When comparing the samples with various OXA3,6 content, indeed we observe that more kebabs are forming in the presence of OXA3,6 over time, correconting to the generating of more kebabs (Figure 9).

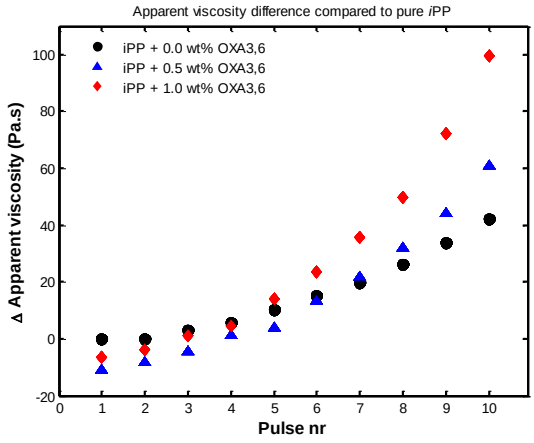


Figure 7. Pressure build-up observed during the consecutive MPR pulses performed on *i*PP containing 1.0 wt% OXA3,6, following the same protocol as shown in Figure 4.

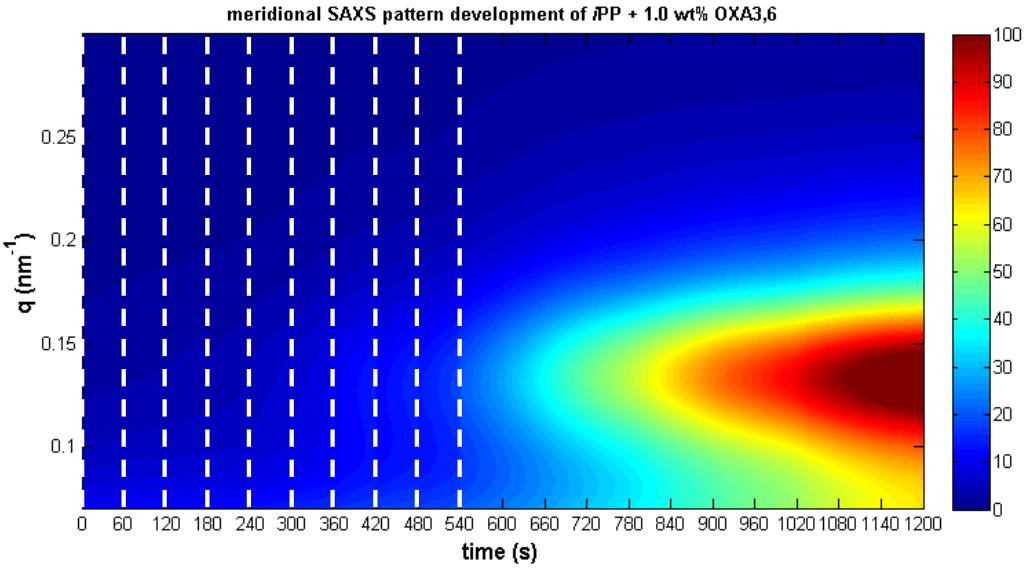


Figure 8. Evolution of Lorents corrected scattering intensity (I·q) in the meridional region, characteristially corresponding to kebab growth. In general, rapid kebab growth is observed during isotherml crystallization at 160 °C after the application of the 10 shear pulses (indicated with the dotted lines). Please note, the kebabs have a L_p, with a long period of 0.13 nm^{-1}.

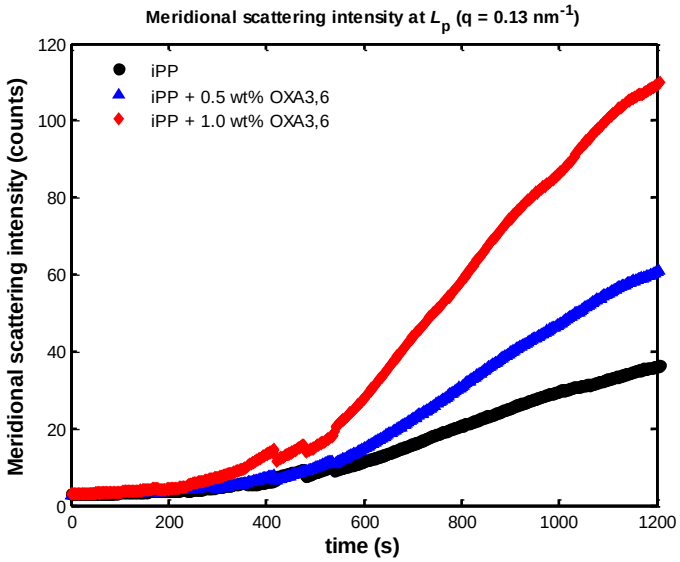


Figure 9. Meridional scattering intensity (at q = 0.13 nm^{-1}) observed during the application of the shear pulses with 1 minute invervals at 160 °C, followed by a 10 minute isotherm.