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Application for beam time at ESRF – Experimental Method

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Aims of the experiment and scientific background

The objective of this study is to contribute to the understanding of the influence of flow gradients on the enhancement of crystallization of isotactic polypropylenes (i-PP's). This will not only lead to a further understanding of Flow-Induced-Crystallization (FIC) of polymers but also will generate the input for numerical models [1-3] and give guidelines for future characterization methods, feasible in standard polymer laboratories, which is indispensable for the application of this knowledge in daily polymer processing practice.

The final crystalline structure in a product determines to a large extend the (long term) mechanical and dimensional properties [5]. This structure is highly influenced by the processing conditions. Besides the usual heterogeneous nucleation, depending on the flow strength, flow induced point-, row- and fiber-like nucleation takes place when the polymer is deformed during shaping processes. It is known that the high molecular weight tail is important in this coupling between the mechanical driven molecular orientation and the nucleation process [1,6]. Therefore, flow strength has to be defined in terms of the highest relaxation time, related to the high molecular weight tail, and the characteristic shear rate of the flow. The product of these two quantities defines the Weissenberg number (We). The complexity of the whole process is increased as the flow induced nuclei act as physical cross-links between the molecules involved. This changes the relaxation times of these molecules which, in turn, changes the visco-elastic flow properties of the polymer and enhances this nucleation process. Therefore, the process of flow-induced nucleation is self-enhancing.

Predicting the final morphology in a product requires numerical modeling that itself needs well characterized and experimentally validated models which should be detailed enough to give the main features of the structures but are simplified to such a level that they are applicable for simulating real shaping processes such as injection molding [2].

Experimental method

The focus is on the comparison of the influence of shear parameters and the thermal history for different i-PP's, i.e. different Mw's and Mw-distributions. Preliminary experiments were done at DUBBLE with a linear and a branched i-PP with nearly the same Mw. For the chosen experimental window (Temperature: 140-165 ºC, shear rate: 2-60 1/sec, total shear: 60-180) it was clearly seen that fibrous structures (shish) formed immediately after shear. At the lower temperature and for the high shear rate the shish are stable (over 30 min) and kebabs grow in the later stage of crystallization together with un-oriented crystals in spherulites. Crystallization after strong flow typically takes place in minutes while, at these temperatures, quiescent crystallization takes hours. At the lower temperature these effects were more prominent for the branched polymer. Surprisingly, at the high temperature the opposite effect is observed; no signs of crystallization are seen in the first 15 minutes for the branched polymer while the linear one shows oriented structures directly after applying shear.

We want to study the early stages of flow-induced crystallization and the related kinetics in more detail in order to get a more quantitative description as required for numerical modeling of these processes.

For a rheological fully characterized i-PP (HD120M0, Borealis), a pure i-PP with a relatively broad Mw, a range of experiments will be performed. This is one of the few i-PP's that is fully characterized, i.e. rheological, thermal and molecular parameter values are available. This allows for an in-depth analysis of the experiments. For example the effect of shear heating can be estimated and the flow strength can be related to the highest relaxation time. Moreover, we have performed in our laboratory an extensive set of rheometric experiments on this material and thus the structure development, as determined from SAXS/WAXS, can be related (indirectly) to the rheological response. The typical timescales of the

crystallization process for given flow parameters and temperature are known from these rheometric experiments.
We will use the Linkam shear cell (CSS 450) in which the shear rate, total shear and the thermal history can be controlled. This shear cell has a plate–plate configuration, i.e. one fixed plate and one parallel rotating plate. This generates a simple shear flow in which the shear rate depends on the radius. The X-ray beam will always pass the sample at the same radius. The cell is equipped with special X-ray transparent Kapton windows making it accessible for X-rays in the gradient direction.
Using the relaxation spectrum as determined in our laboratory different ranges of the applied shear will be examined: a) mild shear for which the (high end) molecules are oriented but not stretched, b) strong flow for which the high end molecules are stretched and fibrous nuclei are formed, developing into shish and, from that, lateral growing kebab (lamella). These regimes are temperature dependent. As the crystallization parameters (nucleation rate, growth rate) are also temperature dependent, a complex interplay of the timescales involved has to be investigated. This implies repeating experiments with the same Weissenberg number (We), which should be based on the highest rheological relaxation time (We_{max}) that is temperature dependent. Experiments will be done for We_{max} values below and above 1, the (maximum) range of temperatures for this type of experiments on i-PP's is typically 130-170 ºC.
To investigate the influence of the high molecular weight tail, which is known to be quite important in FIC, blends will be made via melt blending in a mini twin-screw extruder. These blends will be based on the i-PP described in the preceding and different I-PP's with high Mw and a narrow Mw-distribution [7] of which different fractions will be added. Depending on the fraction, the added high Mw molecules will or will not overlap with each other. In literature it is claimed that in case of no overlap the added fraction is not effective for FIC [8].
We are especially interested in the orientation and transient behaviour of flow induced fibrous structures (shish) for which in-situ 2-D SAXS measurements are required. One experiment on one sample takes two-and-a-half hour (half an hour preparation, two hours measuring). Eight experiments are done on the base polymer (two temperatures, two shear rates, two shear times), and four experiments on each of the blends (four blends, one temperature, two shear rates, two shear times). This takes 60 hours. Together with the installation and calibration time (half a day) this requires 9 shifts.
The evolution of the crystallinity will be determined using 1-D WAXS. A full picture of the final structure will be obtained by applying image plates.

Results expected

We will find whether the expected coil to stretch is indeed determined by a $We_{max} = 1$ and this will determine the onset of fibrous nucleation (shish formation). The stability of these shish will be determined in terms of a survival time. The results from linear, branched and blended i-PP's will give further indications how to incorporate the influence of molecular properties in the kinetic equations that describe the flow-induced crystallization process. Moreover, the important observation, reported in literature, that the rate of flow-induced crystallization increases with an increasing temperature while applying the same stress will be checked. Surprisingly, this increase scales with the rheological relaxation times, i.e. is described by the WLF equation.

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