

## Application for beam time at ESRF – Experimental Method

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### Aims of the experiment and scientific background

The main objective of this study is to use a novel stress-controlled rheometer to study flow induced crystallization phenomena in isotactic polypropylenes (i-PP's) and structure development in SBS block copolymers with a high polystyrene content. The rheometer is designed such that X-rays can pass through the sample in vorticity direction of a simple shear flow, i.e. perpendicular to the plane in which molecules or micro domains are rotated and oriented most strongly. Similar experiments are usually done with the X-ray passing in the gradient direction for which the observable orientation effects are much weaker. Plate-plate (for example sliding plates, the Linkam shear cell, or the adapted Bohlin rheometer [1] with limited strain used at the DUBBLE beam line) and Couette are the most used configurations in that case. Another important difference, when comparing with previous experiments, is that in general structure development under flow is investigated without doing rheometry, i.e. measuring shear and normal stress. This prevents to establish the relation between structure development and applied stresses. The new rheometer can measure shear and normal stresses very accurately (top of the market). Moreover, as this rheometer is stress controlled, startup phenomena that complicate the interpretation of experimental results are avoided. The molecular orientation that drives the flow-induced crystallization process and the morphology orientation in block copolymers, both determining the final mechanical properties [2,3], are attained nearly instantaneously.

**Flow induced crystallization** The final structure in a product determines to a large extent the (long term) mechanical and dimensional properties [3-5]. 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 most important in this coupling between the mechanical driven molecular orientation and the nucleation process [6]. Flow strength, therefore has to be defined in terms of the highest relaxation time, which is related to the high molecular weight tail, and the characteristic shear rate of the flow. The complexity of the whole process is increased as the flow induced nuclei act as physical cross-links that, in turn, change the relaxation time of the molecules involved and thus changes the visco-elastic flow properties of the polymer. This enhances this nucleation process and, therefore, makes the process of flow-induced nucleation 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 simplified to a level that they are applicable for simulating real shaping processes such as injection molding [5].

**Structure development in SBS block copolymers** Recent studies have begun to identify the deformation mechanisms of isotropic di- and triblock SBS copolymers and the influence of morphological anisotropy in macroscopically oriented specimens [7-8]. The most commonly used and studied materials possess a styrene content of less than 30 wt%. Recent studies show more interest in SBS triblock copolymers for which PS is the major component [9-10]. Although, the principal micro deformation process in styrene-based copolymers is crazing, it was suggested that the micro phase separated morphologies in the nanometer scale are too small to initiate crazes. The mode of deformation of styrene based triblock copolymers strongly depends on the morphology and orientation. These materials are perfect model systems to study the influence of long range order and orientation on craze initiation, stability and growth and the occurrence of cavitation and shear yielding. The microdomain morphology, lamellar or cylindrical, has important implications for the deformation behavior.

### Experimental method

A novel stress controlled rheometer (MCR 300 with a modified P-ETD 400 oven) was built by Anton Paar GmbH (Graz, Austria) according to specifications by our group. The rheometer is extensively tested in our laboratory before it is installed at the DUBBLE beam-line. The experiments proposed will be the first one on this rheometer. A postdoc is paid by the Dutch Polymer Institute and posted to the ESRF. He will act as the expert with respect to the novel rheometer and support these experiments. Moreover, our group will post temporary another postdoc, who is an expert in rheometry, to support the first measurements, which will be done during inhouse development time and on machine days. The rotational rheometer has a plate-cone configuration ( $3^\circ$ ) from which only the outer ring of 1 mm is used. By tilting the setup  $1.5^\circ$ , the sample is accessible for the X-ray beam through specially drilled holes and time resolved WAXS and SAXS can be combined with rheometry.

When compared to rheometers that were used at the DUBBLE beamline, the new rheometer has some important advantages. The temperature control allows for relatively high cooling rates, important for crystallization experiments where the crystallization temperature should be reached in short times (minutes for i-PP's). The cooling system is designed such that the homogeneity of the sample temperature is optimized. Next, the strains are not limited, as, for example, is the case for sliding plates and the adapted Bohlin rheometer used at the DUBBLE line that allows only for oscillatory shear, but continuous shear is possible. Finally, the apparatus is stress controlled.

The required measuring time is 12 shifts. This is specified as follows: one day is required to install this new rheometer, perform the calibration procedure and perform the first control tests. Next, we want to repeat a set of measurements as were done on DUBBLE using a modified Linkam shear cell. These concerns shear experiments at different crystallization temperatures, with different shear histories on five different i-PP's. We use one base i-PP with broad Mw and four blends where we add i-PP' with high Mw and a narrow distribution to the base polymer via melt blending on a mini twin-screw extruder. We are especially interested in the orientation and transient behavior of flow induced fibrous structures (shish) for which in-situ 2-D SAXS measurements are required. One experiment takes two-and-a-half hour. 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. 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. Next we plan to perform a set of experiments on a SBS blockcopolymer with 75 wt% PS where in situ 2-D SAXS is sufficient to determine the transients of the structure development. Experiments will be performed at two temperatures, two shear rates, and two shear times, each taking one and half hour, including preparation of the sample.

### **Results expected**

We will get a direct observation of the transient orientation of the structure created during and after flow. We can compare this orientation with the molecular orientation predicted from advanced visco-elastic models (extended Pom-Pom model (XPP)). The XPP-model has shown to be very reliable [11]. We will, therefore, get an indication if, as is assumed in the numerical models, the molecular orientation in the melt is a good predictor for the orientation that are created by the flow and, depending on the shear and thermal history, how stable this orientation is.

### **References**

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