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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Strain-Induced crystallization of semi-crystalline polymer matrix in presence of high aspect ratio fillers.	**Experiment number**: 02 01 759,
Beamline:	**Date of experiment**: from: 13th of march 2009 to:15th of March 2009	**Date of report**: 25th of June 2009
Shifts: 6	**Local contact(s)**: Cyrille Rochas	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In the general frame of material science, and particularly for polymers, it is essential to control the structure of the materials at the nanoscale. As an example, a large number of studies is devoted to the evaluation of the dispersion quality of the nanofiller and its global effect on the properties of polymeric nano-composites. Nevertheless, in some other cases, the nanostructure is not resulting from an extra nanofiller but it is intrinsically due to the polymer supramolecular organization. Hence, semi-crystalline polymers can be conceived as polymer-polymer nano-composites since the crystalline lamellae are generally around 10 nm thick. Many other families of polymers can also be viewed as nano-composites, such as segmented thermoplastic polyurethanes (TPU) which are made of rigid and soft segments, thermodynamically incompatible in a given temperature range, with an order-disorder transition temperature (T_{ODT}). Thus, when these polymers are cooled from the melt, a microphase separation occurs leading to a soft matrix filled by a rigid nano-phase structurally organized from the glassy amorphous to the semi-crystalline states. Obviously, the thermo-mechanical conditions of the nano-structuration will impact the final morphology and the structuration kinetics. That was the object of the present experiment. We performed SAXS experiments on D2AM beamline (experiment n 02 01 759; 6 shifts), in order to follow such structuring mechanisms.

First, using the thermo-regulated sample holder available in the beamline, heating and cooling runs on TPU samples were carried out, especially to follow the structuring of the material from the melt. As an example, Figure 1 shows the scattering patterns obtained during cooling at 4°C/min from 200°C to 100°C (with exposure time of 10 s). The results clearly show that the structuring process is a two steps mechanism. First, from 165°C to ~100°C, the scattered intensity increases but the measured long period is practically constant ($2\pi/q_{max}$~18 nm). The obtained values of the long period are consistent with the lamellar stacks model of semicrystalline polymers that we use in the following for the description of the solidification of the rigid domains. Accordingly, the increase of the scattered intensity during this first step is mainly related to the quantity of the rigid phase as the result of the progressive solidification of preformed (phase-separated) rigid-rich liquid domains or by the coarsening of solid rigid domains. In the second step a mechanism similar to secondary crystallization is evidenced leading to a slow decrease of the long period down to ~14 nm.

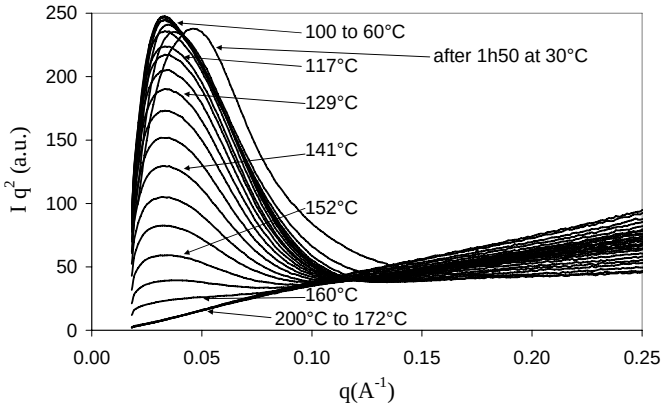

Figure 1: Lorentz corrected SAXS profiles for a TPU cooled from the melt and aged at 30°C.

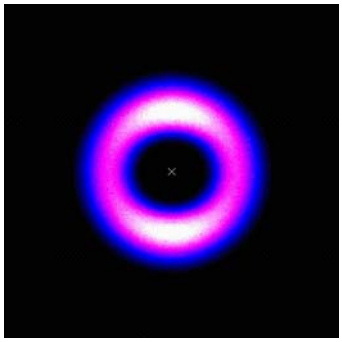

Figure 2: SAXS pattern for a highly sheared TPU. The flow direction is vertical, the crystalline lamellae grow perpendicularly to the vertically-oriented polymer chain.

The specific aim of the study was to investigate how the thermo-mechanical history can generate peculiar morphologies in the material. As an example, Figure 2 shows the 2D-SAXS pattern obtained on D2AM beamline on a small cylinder previously punched out from a plate obtained by injection molding at high shear rates. The anisotropic morphology is clearly evidenced. Thus, it becomes essential to investigate and control the strain undergone by the material during or just before phase-separation and solidification. One of the most suited tools for this task is the shearing hot stage CSS450 supplied by Linkam. After a few technical modifications and adaptations, this device can be positioned in the beam line to follow *in situ* the structuring after or during a shear treatment. Originally, the experimental beam time should have been mainly dedicated to such measurements. Unfortunately, series of difficulties occurred during the experiment which constrained us to significantly reduce the efficient experimental time. The major problems were linked to the failure of an electronic DA device for one part and the failure of the rapid shutter for a second part. Globally these breakdowns took approximately 10 hours to be fixed for a total beam time of 48 hours. In addition,, some unexpected difficulties related to the shearing hot stage itself arose. Indeed, the CSS450 Linkam hot stage needs some alterations to be used with an x ray source, mainly because of silica windows in the original device. For previous experiments (02-01-658, main proposer Prof. G. Régnier) the windows of our shearing hot stage were adapted to allow successful experiments. Depending on the studied materials and/or the type of experiment (SAXS or WAXS), thin aluminum or polyethersulfone, and even sometimes silica windows were used. The design of these windows must meet to several requirements:

- low absorption of the x-ray beam
- low scattering of X-rays
- resistance to high temperatures (>250°C)
- resistance to organic solvents since the windows must be cleaned after an experimental run.
- the used material should allow proper thermal regulation of the device.

However, during the experiment, the different previously designed windows turned out to be badly adapted to TPU which required the use of temperature higher than 200°C and for which the scattered intensity was weak. Indeed, the compromise of glass and PES windows which was successfully used for the crystallization study of polyethylene by SAXS was concluded not to be optimal in the case of our experiment.

Obviously, all these difficulties considerably reduced the impact of the experiment, even if some fruitful results remain concerning the thermal behavior and the morphological orientation of the studied TPU.

From that experiment, new windows for our Linkam device have been designed. Steels plates were positioned in the cell to allow the shearing of the sample. These plates were judicially pierced to allow the x-ray beam path and they were then covered with a kapton film to avoid material leakages from the windows. One of the most difficult points here was to find a glue allowing to work at high temperature, but this problem is fixed now. In our lab, tests of our Linkam device with this new set-up were performed with success at different temperatures and shears in presence of TPU. The windows were also evaluated on the D2AM beamline. Thus, it will be possible to continue *in situ* SAXS experiments while shearing the samples.