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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.

***Published papers***

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:** Semicrystalline texture development in sheared nano-composites. | **Experiment number**: SC-2909, |
|---|---|---|
| **Beamline**: | **Date of experiment**: from: 15th of july, 2010 to: 19th of july, 2010 | **Date of report**: Sept. 1st 2010 |
| **Shifts: 12** | **Local contact(s)**: Cyrille Rochas (D2AM) | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

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## Report:

In the field of the polymer-based nano-materials science, one of the key issue is the control of the dispersion of the nano-filler. Moreover, for most of these materials the processing generally implies large shear or elongation strains which lead to anisotropic morphologies. These oriented structures may be the result of the filler orientation if it presents a high aspect ratio but also of the polymer matrix itself which can be intrinsically biphasic (semi-crystalline, block-copolymer, segmented copolymer…). This project is devoted to the elaboration and analysis of nano-composites with nano-fillers of large aspect ratio. This project which began at the end of 2009 is supported by the French Research National Agency (ANR) in the framework of "Programme BLANC - Projets interdisciplinaires" : Crystalline Orientation in Polymers from Inorganic Nanofiller (COPIN).

Basically, in the present experiment, *in situ* SAXS and WAXS measurements were performed on sheared melt polymer based nano-materials with a semi-crystalline matrix. These analyses were carried out by means of a CSS450 shearing hot stage provided by Linkam Scientific Instruments LTD which had been previously specially adapted for our study. Hence, owing to the short exposure times (~1 s) achievable with the use of a high brilliance x-ray source beamline (D2AM), we could follow the filler reorientation but also the matrix crystallization.

Since the analysis of the experiments is still under progress, only preliminary conclusions will be drawn in the present report. Nevertheless, some important results can be highlighted concerning topics like the crystallization kinetics of the polymer matrix, the crystalline orientation, the influence of the fillers…The results shown further are dealing with materials based on isotactic polypropylene (PP) matrix filled or not with high aspect ratio talc particles.

In Figure 1, SAXS and WAXS images are displayed for sheared and non sheared virgin PP. When applying a short-term shear treatment to the melt polymer at 140°C, the diffraction rings of the α crystalline phase of PP are clearly observable after 5 minutes whereas, at this time, the non sheared PP is practically not crystallized yet. Concomitantly, in the SAXS pattern at 5 minutes, the (anisotropic) correlation bump is already noticeable whereas it is hardly visible for the non sheared sample. Hence, the crystallization kinetics enhancement due to the shear treatment can be characterized quantitatively from these experiments.

Moreover, Figure 2 shows the azimuthal variation of the diffracted intensity for (110) and (040) planes of the α crystalline cell of PP for different crystallization times. The revealed crystalline orientation corresponds to a twofold types of crystalline lamellae, *i. e.* one with the *a* axis of the unit cell oriented in the

direction normal to the plane and another with the *a* axis oriented in the flow direction. Moreover, thanks to the *in-situ* following of the crystallization, it can be concluded that this twofold orientation is obtained from the beginning of the crystallization since the growing of the maxima around 90° and 270° are simultaneous with the growing at 180°.

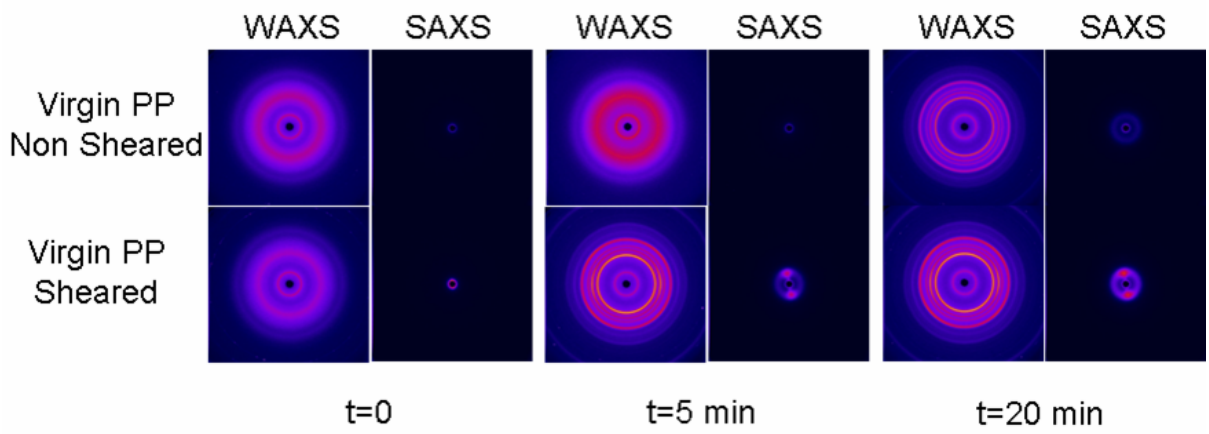


**Figure 1:** Evolution with time of WAXS and SAXS patterns obtained for Virgin PP at 140°C with or without a short term shearing treatment (shear rate of 20 $s^{-1}$ during 11 s, the flow direction is vertical).

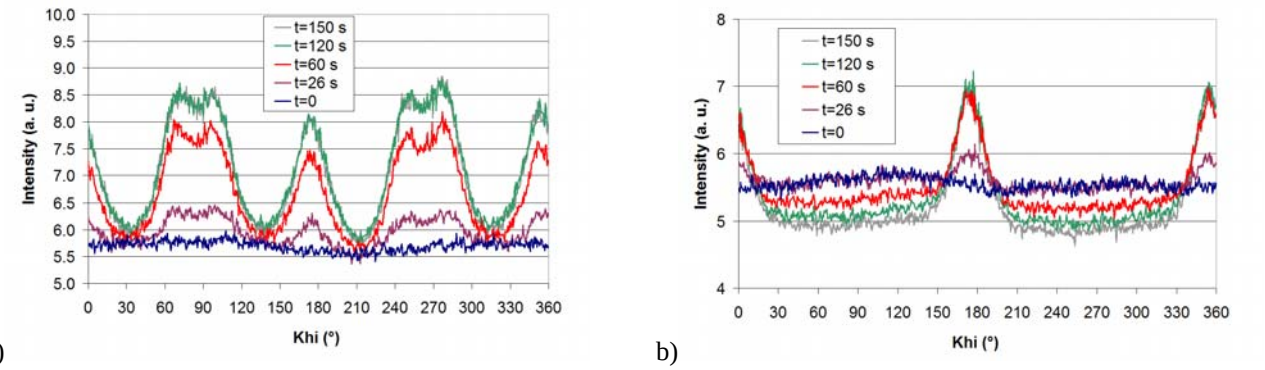


**Figure 2:** Azimuthal variation of the diffracted intensity for the 110 (a) and 040 (b) planes of PP α crystalline phase for a blend PP/talc (90/10). The shear treatment was 60 $s^{-1}$ during 5 s. The flow direction is at Khi=90°.

The effect of the filler on the obtained superstructure represents another important issue of the experiment. Figure 3 shows the azimuthal variation of the partial invariant which is the sum of $I.q^2$ over the $q$ range corresponding to the correlation bump due to lamellar stacks of the PP crystallites. For the same shear treatment, the amount of lamellar stacks in Bragg conditions is higher in the presence of the nucleating filler but the obtained orientation of the superstructure is much less pronounced.

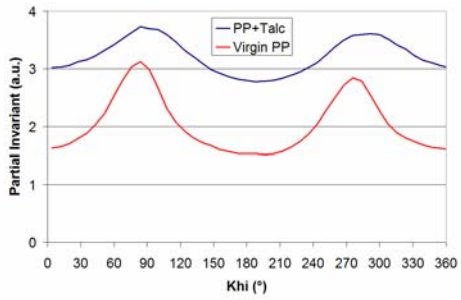


**Figure 3**: Azimuthal variation of the partial invariant ($\Sigma Iq^2$) for virgin and filled PP submitted to a short term shearing treatment (shear rate of 20 $s^{-1}$ during 11 s, T=140°C). The flow direction is for Khi=90°. The pictures were taken 20 min after the shearing

During this experiment, many other systems were studied like, for example, Polyethylene with Phosphate–glass or polypropylene with $SiO_2$ particles which were previously generated and elongated directly in the matrix. As a whole, our methodology is now undoubtedly operational for such *in-situ* measurements for melt polymers submitted to a shearing treatment. A wide type of experiments can be achieved allowing some breakthroughs in the knowledge of the material behavior during its processing. However, some improvements in the experimental setup are foreseen in order to have an even better thermal control of the sample and also a broader range of shearing treatments.