ESRF	**Experiment title:** Micro and Macro true mechanical behaviour correlation for thermoplastics by WAXS/SAXS and Raman analysis	**Experiment number**: MA 5544
Beamline: BM 26	**Date of experiment**: from: 14/02/2023 to: 17/02/2023	**Date of report**: 25/05/2023
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Objective of the project:

This study covers the physical mechanisms of deformation in semi-crystalline polymers. It aims at correlating the true macroscopic mechanical behaviour of these materials with the evolution of the stress and strains fields at the microstructural scale, in both the amorphous and crystalline phases. The whole viscoelastic and plastic domains are studied, for glassy and rubbery initial states. Two polyesters are selected as the main investigated materials: the Poly(ethylene terephthalate) (PET) and the Poly(ethylene furanoate) (PEF), a new biosourced and still not well studied material. These two polymers can actually present either a fully amorphous or a semi-crystalline microstructure, only by controlling the initial processing. This characteristic can therefore help to separate the contributions of each phases.

Experimental techniques:

Synchrotron X-ray scattering techniques have been chosen to investigate the aforementioned phenomena, considering the spatial scale at which they occur. All measurements were realised in situ on small tensile test specimens stretched with a portable stress rig equipped with a heating cell. Both WAXS and SAXS measurements were realised for this study. Analysis were performed with an incident beam energy of 12 keV.

WAXS patterns contain information on both amorphous and crystalline phases. The crystalline phase is visible in the form of diffraction rings. The strain and stress states of this phase can be calculated by applying the $\sin^2 \psi$ method on the positional shifts of the diffraction rings during the sample straining. The X-ray scattering by the amorphous phase creates on the pattern a halo whose shape gives information on the strain state of this phase.

SAXS patterns show information at a larger spatial scale, and thus allow the quantification of the evolution of the so-called “long period”, i.e. the average distance length of the stack of a crystalline lamella and an amorphous zone for semi-crystalline polymers. This information is needed to analyse the interactions of the two-phases.

WAXS and SAXS measurements were realised separately to collect all the scattering data on the full frame of the PILATUS detector. WAXS patterns with a complete 360° azimuthal range are needed to analyse the texturisation of our samples and to precisely measure the positional shifts of the diffraction rings.

Raman spectroscopy allows the study of both crystalline and amorphous phases. The materials' stress states can be quantified with the Grüneisen method by measuring the vibrational bands positional shifts. Raman spectroscopy is realised in our laboratory, in situ, on the same kind of specimens strained with the same conditions as the ones used during our experiment at the ESRF. The Raman data are then correlated to the WAXS/SAXS ones

<u>Preliminary results:</u>

The planned experiments were successfully completed. PET and PEF in their amorphous and semi-crystalline states were analysed, below and above the glass-transition temperature. A significant number of experiment were focused on cyclic mechanical tests.

Figure 1 shows the type of WAXS pattern obtained during the in-situ tensile tests. For amorphous and semi-crystalline PET at high temperature, this example exposes the apparition of a mesophase at high strain, among other information.

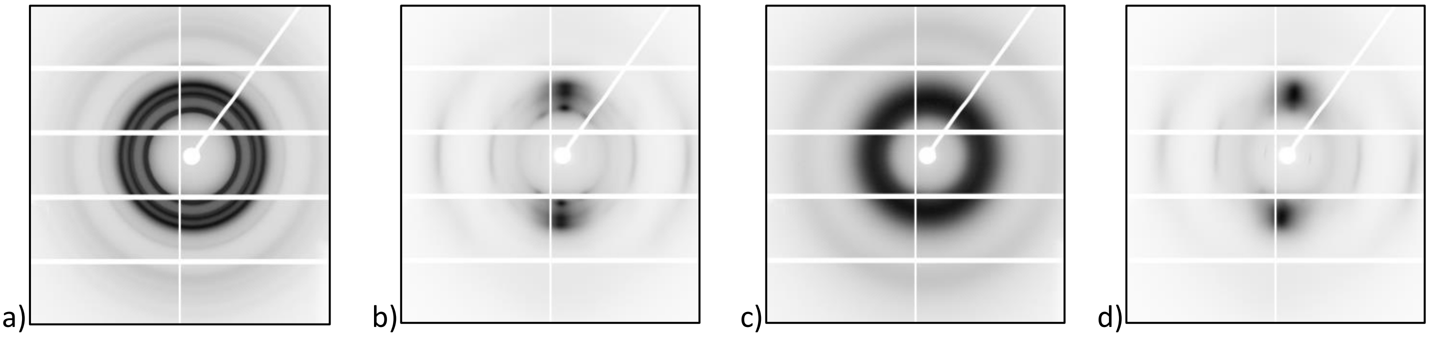

Figure 1: WAXS patterns for several samples in different conditions. Elongation is applied horizontally Semi-crystalline PET (crystal. ratio:26 %),105°C: a) no deformation; b) deformation > 1. Amorphous PET, 85°C: c) no deformation; d) deformation >1

Figure 2 illustrates the evolution of the long period for the semi-crystalline PET during deformation.

By optimising our time during this experimental campaign, we were able to study a few samples from other polymers (PVDF and Polyamide). The data obtained from these experiments will serve as references to prepare other synchrotron proposals. A few specific measurements on the structural changes of epoxidised natural rubber with conductive carbon black loading were realised as well.

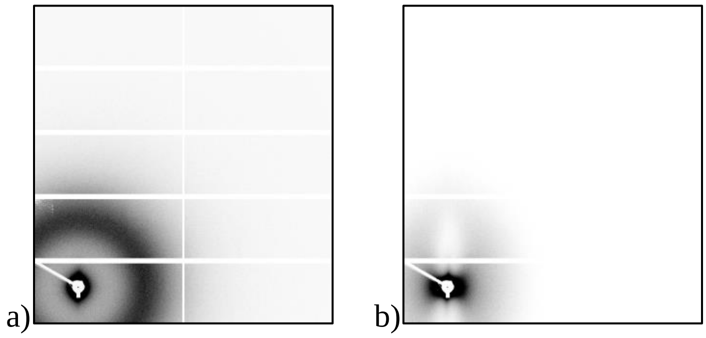

Figure 2: SAXS patterns for PET in semi-crystalline state (crystal. ratio 26%) at 105°C. a) no deformation; b) deformation >1

At the time of the deposit of this experimental report, all these data are still under investigation. For PET and PEF, a publication on the evolution of the mesophase under mechanical loading is in preparation.