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

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

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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.

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this study we have recorded both WAXS et SAXS patterns during uni-axial deformation of Poly(lactic acid) (PLA) and Polyethylene (PE) using the Princeton CCD camera available on the BM02 beamline and a stretching device designed so as to be adapted on this beamline. In this report we will describe the results obtained, on the one hand for the deformation of the PLA samples on a large temperature range and on the other hand for PE with different molecular architectures when stretched at room temperature.

Regarding to the PLA, the resin used in this study has a 4.3% D-isomer content and the samples were stretched at $\varepsilon° = 0.01s^{-1}$ in the temperature range 25°C-75°C. Both amorphous and semi-crystalline films (χ_c = 5% & 28%) were studied in order to characterize the influence of crystallinity on the structure evolution.

Drawing experiments in the range 45°C-65°C, *i.e.* up to or near the glass transition temperature Tg, have allowed us to give evidence that whatever the crystallinity a mesomorphic phase, *i.e.* a phase with an intermediate order between amorphous and crystalline phases, is induced upon stretching, as it has never been reported before. Figure 1 illustrates a typical WAXS pattern and the associated intensity profile of the mesomorphic phase.
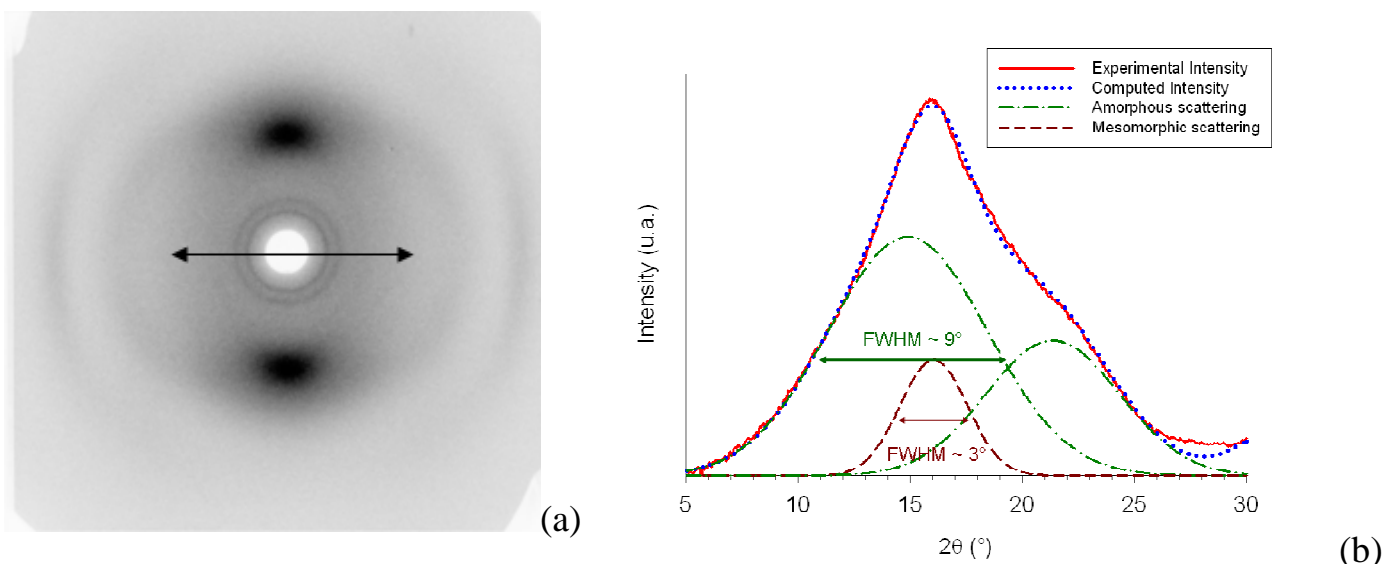
(a)

(b)

Fig 1 : Typical WAXS pattern of a mesomorphic sample (a) and associated deconvolution of the azimuth- integrated intensity profile (b)

The mesophase content was calculated as a function of deformation. A direct correlation was established between the development of the mesophase and the strain hardening phenomenon occuring at high strain levels. On the other hand the results obtained for the stretching at Td = 75°C have shown that the observed strain hardening phenomenon results from an actual strain-induced crystallization phenomenon.

Examination of the integrated intensity profiles obtained at Td = 75°C revealed that the structure of the induced crystalline phase differs from the structure of the thermally cristalline phase as can be seen on Figure 2. The "strain-induced crystal" consists in a slightly distorted form of the "thermal crystal". The observed differences can be ascribed to the D-isomer content of our material. Indeed during thermal crystallization the D- isomer units can be easily excluded from the cristal lattice contrary to stretching that compells to incorporate the crystal lattice.

Another issue of those experiments was to understand the role of the mesophase. In this way we followed the structure evolution of a sample with a significant mesomophase content during relaxation and heating experiments.

Fig2 : Comparison of the intensity profile obtained for a thermally induced crystalline and a mechanically induced crystalline sample

The obtained results strongly suggest that, contrary to the case of PET, the mesophase in PLA does not act as a precursor of crystallization but rather correspond to constrained oriented chains which are unable to crystallize due to lacking mobility. Nevertheless this conclusion has to be confirmed by further investigations.
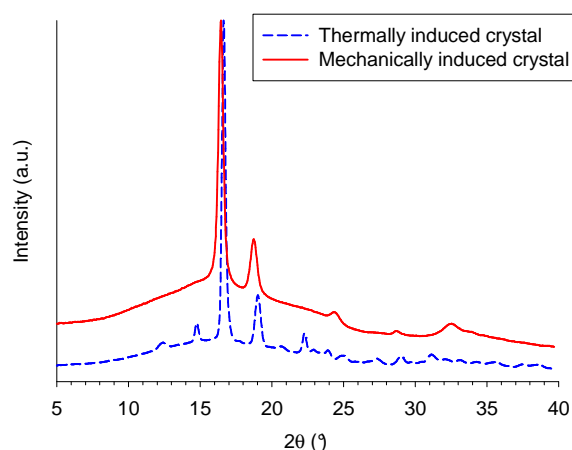
The SAXS experiments carried out on the samples were aimed at characterizing the structure evolution of the material at a mesoscale in combination withWAXS experiments.

For samples stretched below the glass transition temperature of the material, SAXS experiments have allowed to follow the evolution of the deformation mechanisms which occur during the deformation. As an example, these experiments revealed that two deformations mechanisms, namely crazing and shear banding, are cooperatively activated as can be seen from the meridian and diagonal scattering respectively in the SAXS pattern from Figure 3.

For draw temperatures above Tg, the SAXS experiments have shown that a long range order builds up for crystallization takes place (Fig 4.a).

Fig3 SAXS pattern of a PLA sample drawn at Td = 45°C (The draw axis is horizontal)

However, no long range order could be observed for Td = 65°C, *i.e.* when a mesomorphic form is induced.

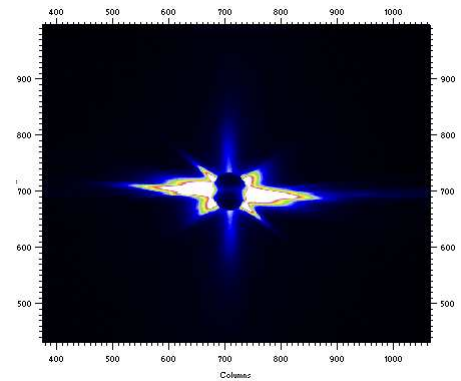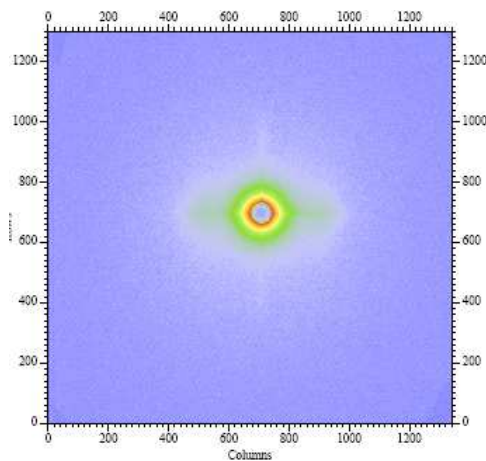Fig 4.a SAXS pattern of an amorphous sample drawn at Td = 75°C at ε = 300% (draw axis is horizontal)
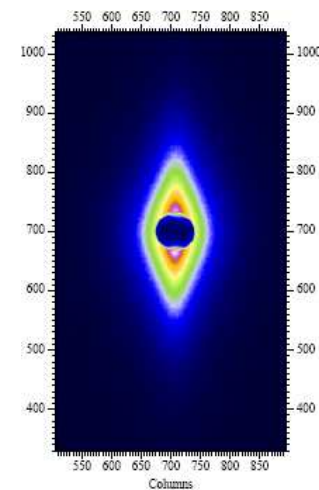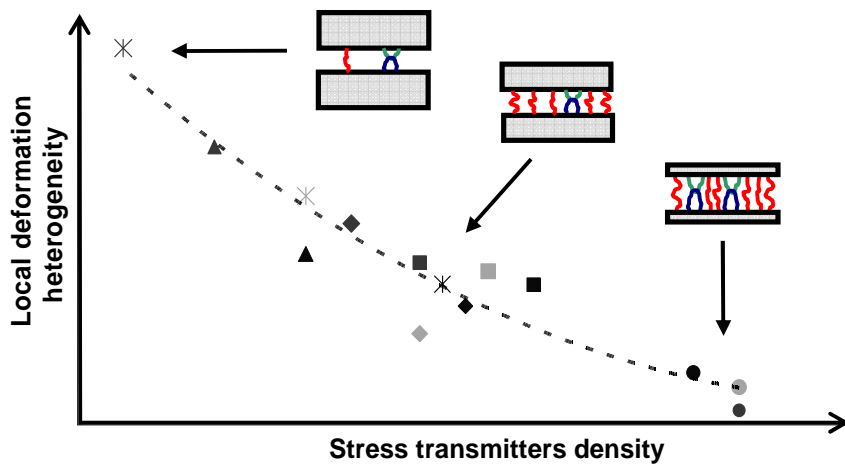
Fig 4.b SAXS pattern of a semi-crystalline sample drawn at Td = 75°C at ε = 300% (draw axis is horizontal)

For initially-crystalline samples, it has been shown that a fibrillation process (Fig 4.b) occurs beyond a deformation of 133%. This latter phenomenon is of prime importance to account for the variations of the crystallinity during the WAXS experiements. Nevertheless for technical reasons the evolution of the long period during the stretching of initially crystalline samples could not be followed.
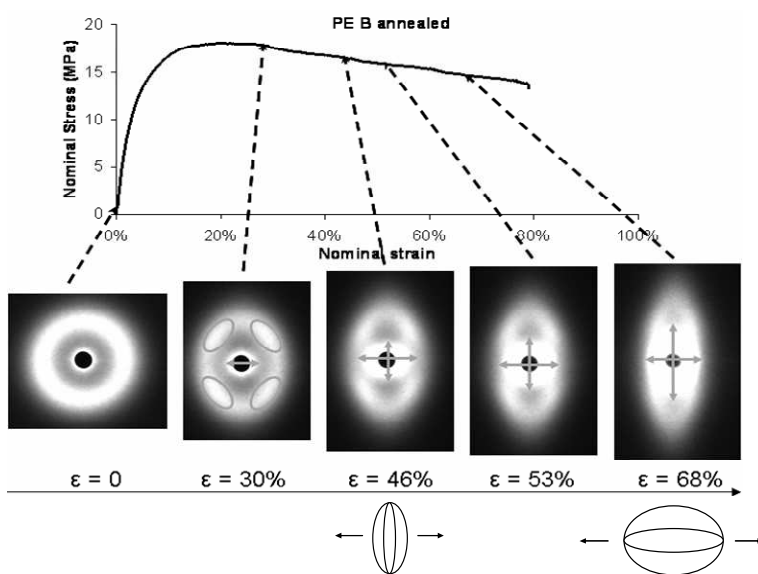
To sum up, the precise characterization of the structure evolution during these experiments has allowed us to explain the deformation mechanisms of the material, in terms of relaxation time and orientation of the amorphous phase which proved to govern the material behavior. A microscopy study is in progress in order to complete the obtained for the initially semi-crystalline samples that display quite complex structure evolution.

Concerning the PE, its visco-elastic behaviour is generally attributed to the amorphous lamellae deformation. Stack lamella deformation depends on their orientation with respect to the loading axis. The local deformation is controlled by the dimensions, the intrinsic properties of the amorphous and crystalline lamellae, and the mechanical coupling between both phases. This coupling is ensured by the stress transmitters (ST) such as the tie molecules and entanglements. The influence of the ST density on the spherulite deformation has been investigated. A wide experimental campaign has been undertaken on several polyethylenes with controlled molecular parameters and subjected to different thermal treatments. The ST density has been evaluated experimentally by the natural draw ratio.

The local deformation until yielding is analyzed by small-angle X-ray scattering along a tensile test thanks to an in situ tensile device specially developed for ESRF.

Fig.5. Local deformation heterogeneity versus the stress transmitters density and the schematic representation of the microstructure of the different samples.

The follow-up of the evolution of the stretching of the long period in the tensile direction has allowed calculating the local deformation of the amorphous phase. The difference between local and macroscopic deformation, that transcribes the heterogeneity of the deformation, was found to be well correlated with the ST density (See fig.5).

Fig.6. Evolution of the SAXS patterns along the tensile for an annealed PE.

The phenomenon of cavitation has also been studied.

Several polyethylenes were found to exhibit voiding. The follow-up of the intensity scattered by the voids along the tensile test has allowed analysing the evolution of the cavities (see fig.6). The analysis of the SAXS patterns has allowed quantifying the size of the cavities and the total volume of the voids. The initiation of voiding and the voiding rate were found to be correlated with the microstructural parameters.

Communication of the obtained results :

<u>International conferences :</u>

G. Stoclet, R. Séguéla, J.-M. Lefebvre, *APS 2009, American Physical Society, March Meeting 2009, Pittsburgh, 16-20 Mars 2009.*
"Structural evolution under uni-axial drawing of poly(D,L lactide) films".

G. Stoclet, R. Séguéla, J.-M. Lefebvre, *Polychar 17, Polymer characterization 17th congress, Rouen, 20-24 Avril 2009.*
"Influence of the crystal content on the drawing behaviour of PLA".

S. Humbert, O. Lame, J.M Chenal, G. Vigier**, *DYFP, Kerkrade, the Netherlands (April, 5-9, 2009)*
« Role of the molecular network on small strain behaviour of polyethylene: SAXS measurements during tensile tests. »

S. Humbert, O. Lame, J.M Chenal, G. Vigier**, *EPF09, Graz, Austria (July, 12-17, 2009)*
« Influence of processing parameters on the local deformation of polyethylene. »

<u>National conferences :</u>

S. Humbert, O. Lame, J.M Chenal, G. Vigier**, *DEPOS 22, La Colle sur Loup, France (March, 18-20, 2009)*
« Influence du couplage mécanique entre phase amorphe et phase cristalline sur la déformation viscoélastique du polyéthylène. »

<u>Publications :</u>

Stoclet G., Lefebvre J.-M., Séguéla R.
In preparation
Time-resolved characterization of the strain-induced molecular ordering of Poly(lactic acid) under uniaxial stretching

S. Humbert, O. Lame, J.M. Chenal, C. Rochas, G. Vigier
To be submitted
« Influence of the molecular network on local deformation: SAXS measurements during tensile tests. »

S. Humbert, O. Lame, J.M. Chenal, C. Rochas, G. Vigier
In preparation
« Influence of the molecular and microstructural parameters on voiding: SAXS measurements during tensile tests. »

<u>Posters :</u>

R. Séguéla, G. Stoclet, J.-M. Lefebvre, C. Rochas, *GFP 2009, Colloque Groupe Français des Polymères, Lyon, 25-27 Novembre 2008.*
"Comportement mécanique et évolution structurale du Poly(acide lactique) en relation avec la déformation plastique".