

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.



	Experiment title: In-situ study of the strain-induced structural evolution of Poly(lactic acid)/Montmorillonites nanocomposites	Experiment number: SC2903
Beamline: BM02	Date of experiment: from: 13/07/10 to: 15/07/10	Date of report: 11/01/11
Shifts: 6	Local contact(s): C. Rochas	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this study we have recorded WAXS & MAXS (Wide & Middle Angle X-Ray Scattering) patterns during uni-axial deformation of Poly(lactic acid) nanocomposites on the BM02 beamline using a homemade powerful stretching device allowing analyzes through the edge and the face, and designed so as to be adapted on the beamline. Different types of nanocomposites were studied :

- on the one hand PLA nanocomposites filled with different clays. Seven types of clays treated with different kinds or no surfactants (Cloisite30B, Cloisite20A... Montmorillonite...) were used. These fillers are composed of a stacking of clay platelets between which is located the surfactant having different nature and chain lengths. The materials were elaborated using a melt-extrusion process.
- On the other hand, PLA nanocomposites based on carbon nanotubes (CNT) were elaborated using a solution route. CNTs have been chosen as this type of filler has received an increasing interest due to specific properties such as electric conductivity and high stiffness.

This report describes the main results regarding the influence of the nature of the filler on the strain-induced structural evolution of the polymer matrix. A wide temperature range above the glass transition temperature of PLA ($T_g \approx 60^\circ\text{C}$) was investigated, the stretching

rate being set at $0,01 \text{ s}^{-1}$ as in our previous study for the sake of comparison (Macromolecules, 2010, 43, 7228)

The first part of this study was the characterization of the structure and morphology of the initial materials. The MAXS/WAXS analysis revealed that all the samples exhibit an intercalated morphology whatever the nature of the filler. Only the clay inter layer distance was modified depending on the nature of the filler. From a structural point of view the WAXS patterns have shown that filled or unfilled samples were initially amorphous.

The observations of the sample structure through the face and width show that:

- in the case of clay fillers, the tactoids were preferentially aligned along the sample thickness, i.e. all samples exhibit orthotropic symmetry (see fig1).
- in the case of carbon nanotubes filler, there was an isotropic distribution of the CNTs.

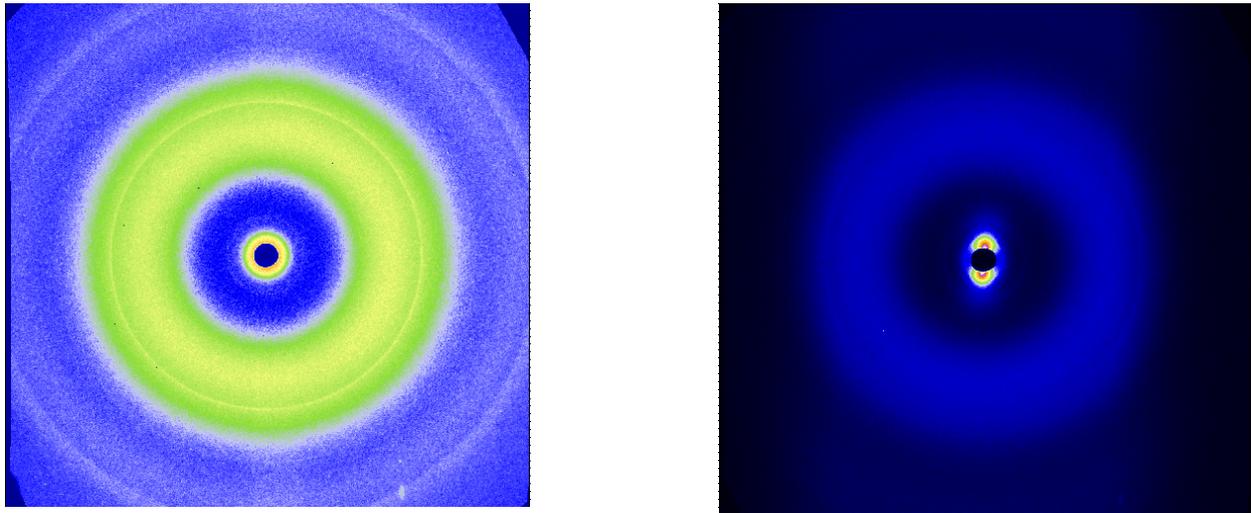


Fig1: (a) Flat-on & (b) Edge-on WAXS patterns of PLA/C30B samples

Regarding the structural evolution of PLA nanocomposites upon stretching as a function of the draw conditions, several behaviors should be pointed out.

First, for a draw temperature near T_g , i.e. $T_d = 65^\circ\text{C}$, we previously demonstrated that a disorder to order transition occurred upon stretching for neat PLA, the ordered phase being a mesomorphic form. In this study we have shown that the filler has no impact on this strain-induced structural evolution regarding the formation of a mesophase. Moreover, the amount of strain-induced mesophase is approximately the same as for neat PLA. Nevertheless, the mechanical behavior shows a reinforcement characteristic of the filler effect..

We have previously shown that there is a link between the nature of the strain-induced ordered phase and the chain dynamics. Thus, this insensitivity of the polymer matrix structural evolution to the presence of filler indicates that the clays or the carbon nanotubes do not significantly influence the polymer chains dynamics.

The second draw temperature in this study was $T_d = 75^\circ\text{C}$, i.e. a temperature for which strain-induced crystallization has been observed during drawing. It has appeared that the presence of the filler does not significantly influence the strain-induced structural evolution of PLA (figure 2), as for the case $T_d = 65^\circ\text{C}$. The fact is that strain-induced crystallization is slightly promoted by the clay, probably due to the so-called shear amplification effect.

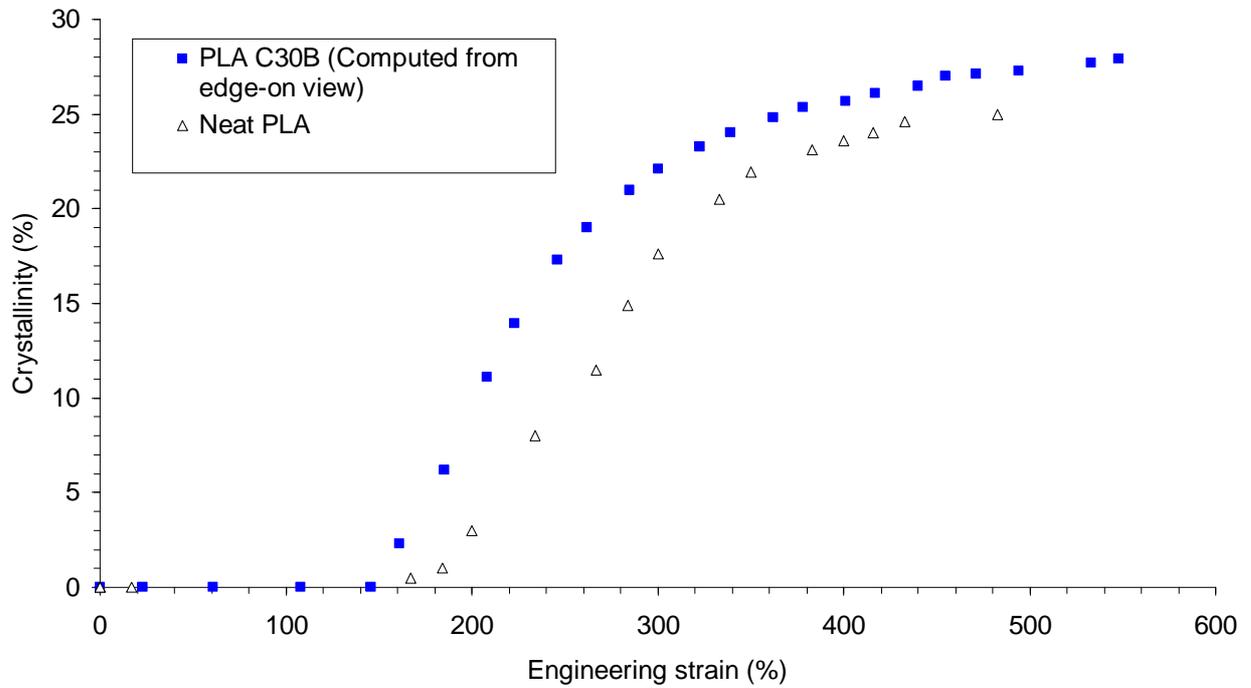


Fig2: Evolution of crystallinity as a function of the deformation at Td = 75° for neat PLA and PLA/C30B nanocomposites

The third draw temperature investigated in this study was Td = 90°C. In this case, a clear influence of the presence of the filler was put in evidence. Indeed, whatever the filler used, a sharp enhancement of the strain-induced crystallization kinetics is observed. This phenomenon start at the onset of the deformation for the nanocomposites, while it only starts at a strain $\epsilon \approx 300\%$ in the case of the neat matrix as seen on figure 3.

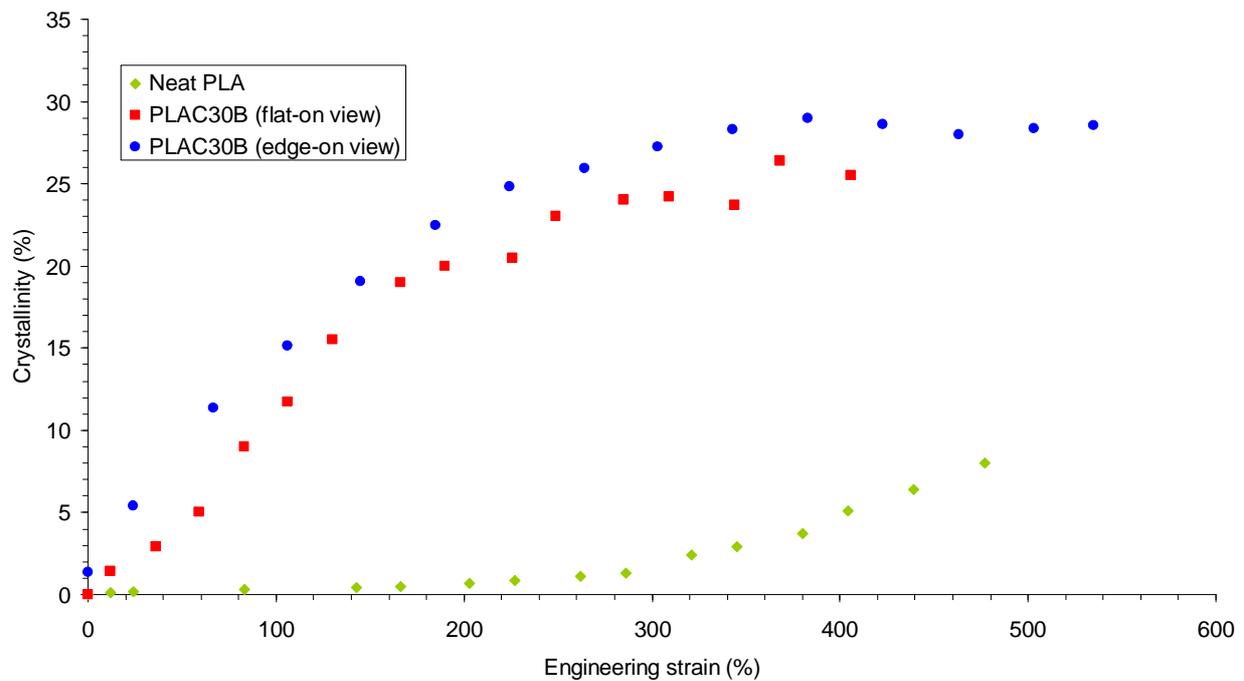


Fig3 : Evolution of crystallinity as a function of the deformation at $T_d = 90^\circ$ for neat PLA and PLA/C30B nanocomposites

This nucleating effect of clay has already been observed in the case of thermal quiescent crystallization but, to our knowledge, it has never been reported for strain-induced crystallization.

More surprisingly, a fine analysis of the WAXS patterns obtained at the beginning of the deformation, (an example is reported on figure 1) indicated that the strain-induced crystals grow with the chain axis normal to the draw direction. This is particularly unusual since the strain-induced crystals are generally oriented with the chain axis along the draw direction.

This quite fast increase of crystallinity for $T_d = 90^\circ\text{C}$ suggests that the nucleating effect of clays combines with the shear amplification effect during drawing. Further work is necessary to progress in the understanding of this process.

An other goal of this study was to assess the potential occurrence of a “strain-induced exfoliation mechanism”. Indeed there are some disparities in the literature regarding to this subject, and knowing the implications that it can have from both fundamental and applied point of view, the latter has to be assessed.

In this aim the Middle Angle Scattering region was meticulously analyzed, as it is the region of clay scattering. Indeed, it is expected that if such a mechanism occurs during drawing one may observe a change in the position, shape or intensity of the diffraction peaks. Surprisingly, no changes in the diffraction peaks are observed even in terms of position than in terms of shape. Quantitative exploitation of the intensity has revealed to be very delicate due to the samples orthotropy.

This behavior can be reasonably explained considering that there is little affinity between filler and matrix, as revealed by the WAXS study.

Nevertheless, to go further, SAXS experiments on polymer nanocomposite systems having

different initial morphologies are envisaged to better assess the existence of the exfoliation mechanism.

Moreover, using the MAXS patterns, it has been possible to determine the orientation factor of the fillers as a function of deformation and draw conditions as illustrated on figure 4.

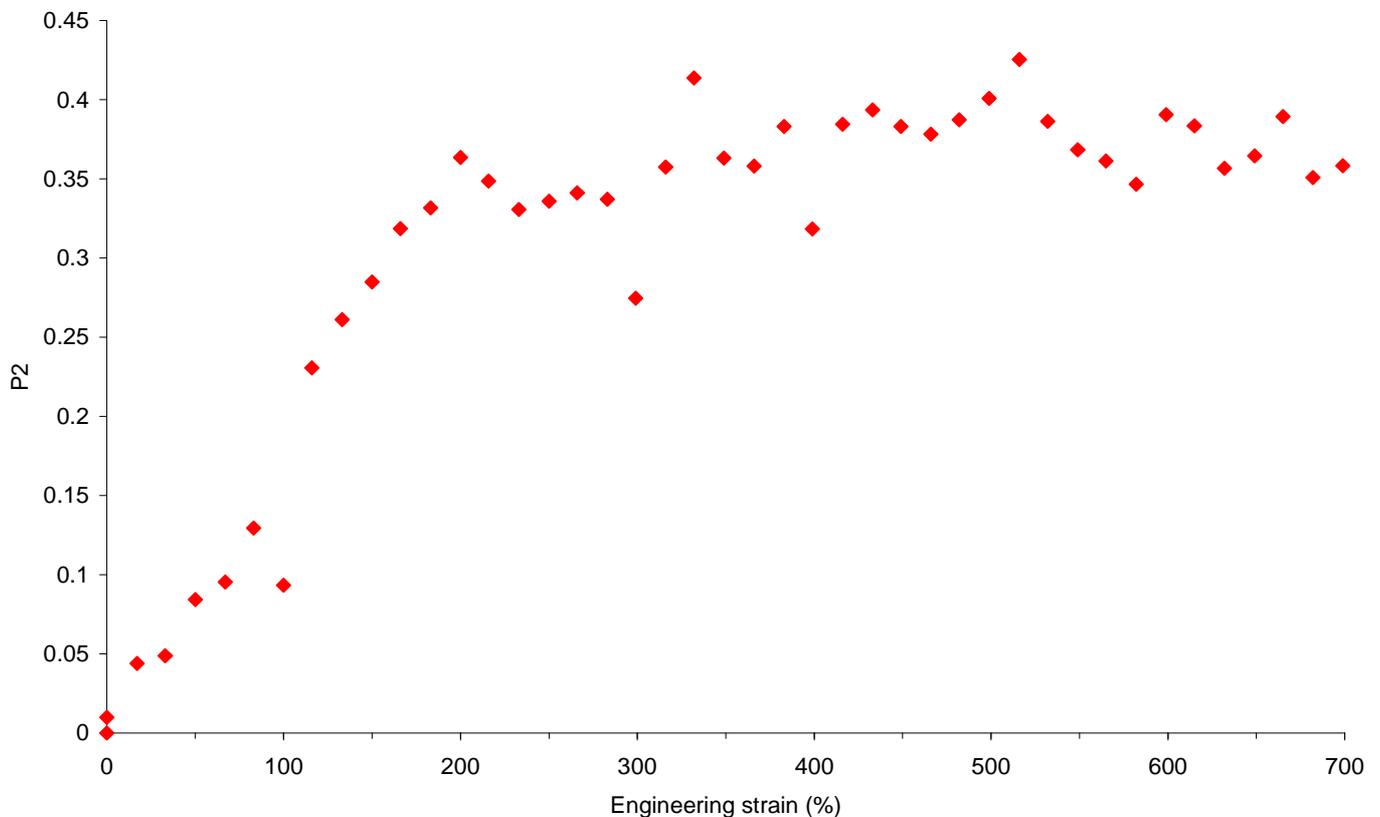


Fig4: Evolution of the orientation factor P2 as a function of the deformation for PLA/C30B nanocomposite drawn at $T_d = 75^\circ\text{C}$

It has been shown that the evolution of the filler orientation was almost the same whatever its nature, but was strongly sensitive to the temperature. Furthermore these data will constitute a precious database for a recent collaboration dealing with the simulation of the mechanical behavior of PLA/nanocomposites.

During this session two concomitant topics were also addressed. On the one hand an attention has been paid to the influence of physical aging on the mechanical behavior of PLA above its glass transition temperature. Indeed, physical aging, which is a phenomenon occurring below T_g , is generally erased when the material is heated above T_g . But it has been recently shown that in the case of PLA a memory of thermal history is kept above T_g as judged from the influence on the crystallization behavior of the material. To explain the latter it has been postulated that some ordered domains are generated during the aging process, but this need further confirmation.

Then, we have investigated the strain-induced structural evolution of aged and unaged PLA stretched above T_g . We have shown that both mechanical behavior and structural evolution are significantly influenced by the aging process. More precisely, aged PLA exhibits faster crystallization kinetics as can be seen on figure 5, and concomitant stronger strain-hardening.

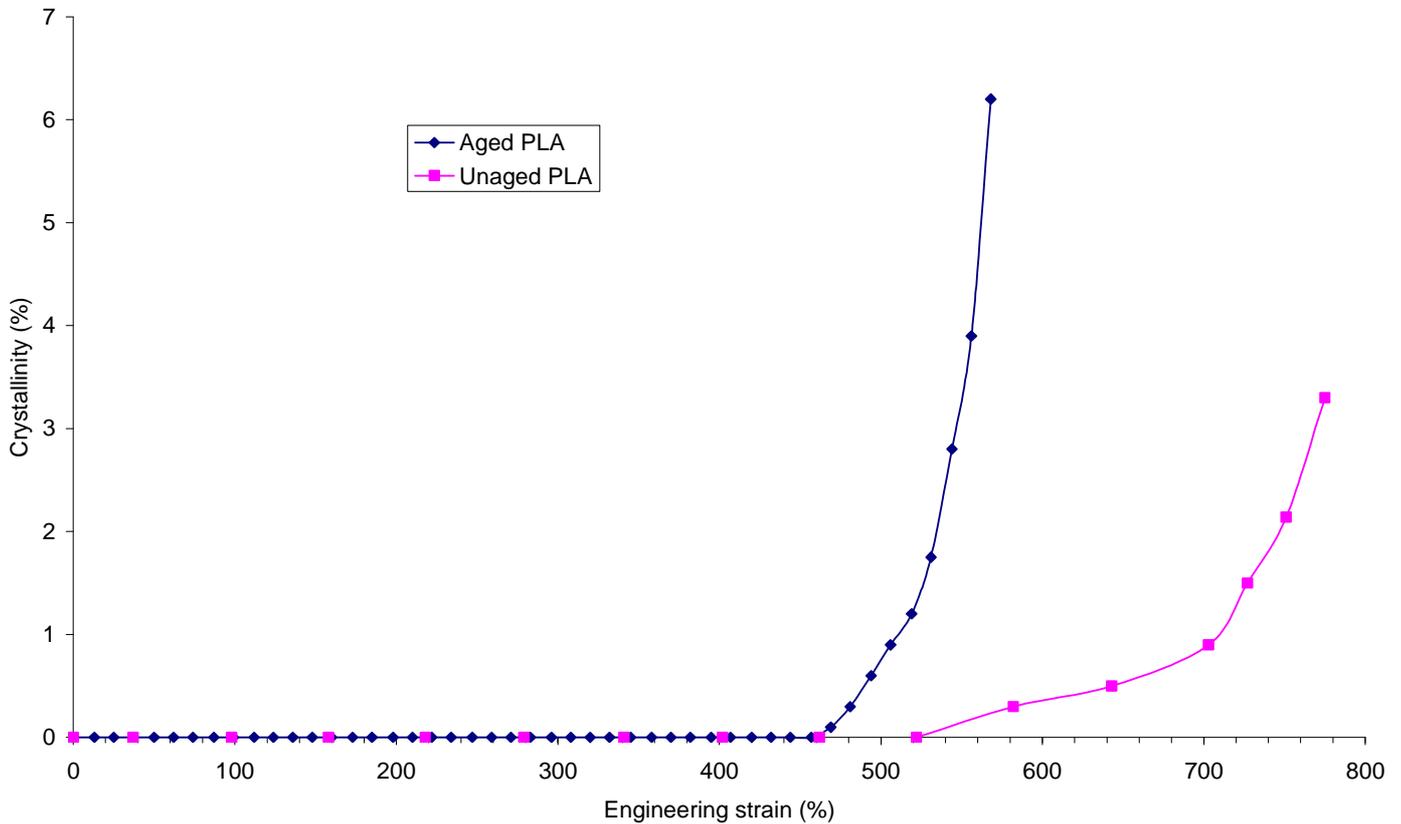


Fig5 : Evolution of the crystallinity as a function of deformation at 85°C for aged and unaged PLA drawn

This is an indirect evidence of the formation of ordered domains during aging, which are preserved at temperatures above T_g , and which plays the role of nucleating agents..

The effect of the D-isomer content on the strain-induced structural evolution has been studied. Although it has been shown by some authors that this parameter has a strong influence on the thermal crystallization behavior of polylactide, there are no studies dealing with the effect of the D-isomer content on the strain-induced structural evolution. Samples covering a wide range of D-isomer contents (from 2% to 50%) have been studied and it has been shown that (see fig6):

- as for thermal crystallization, it exists a critical D-isomer content above which no crystallization is possible.
- Contrary to the case of thermal crystallization, the kinetics of strain-induced crystallization is not sensitive to the D-isomer content for the samples able to crystallize. This means that chain orientation governs the process.
- Only the samples able to crystallize are able to form a mesomorphic phase when stretched near T_g , demonstrating that the PLA mesophase is a precursor of the crystalline phase.

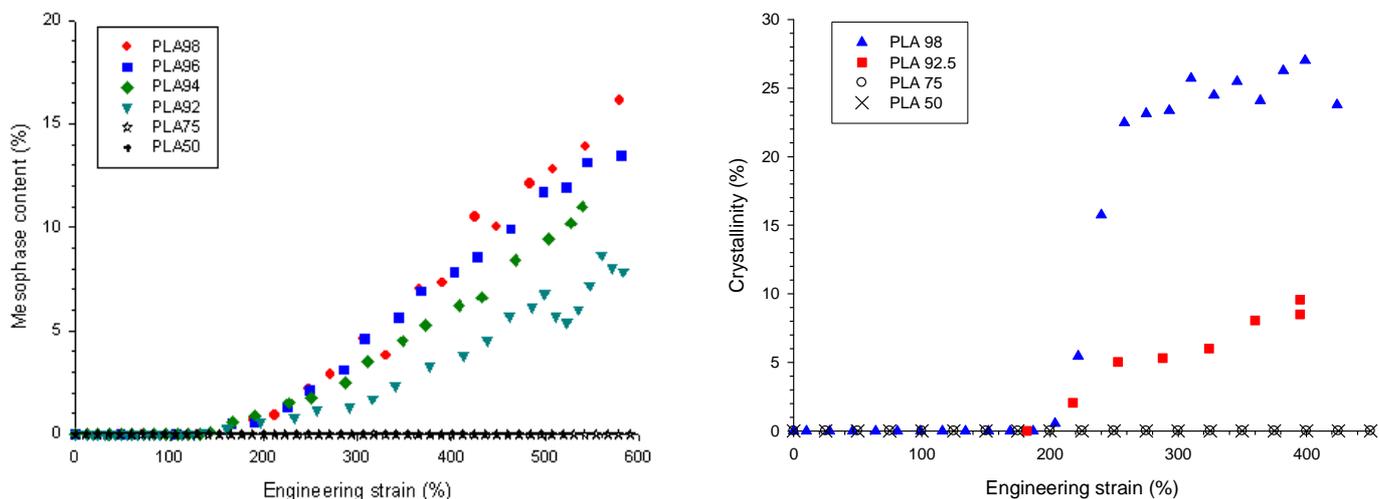


Fig6 : Evolution of the ordered phase content as a function of deformation for PDLLAs with various D-isomer contents drawn at (a) $T_g + 5^\circ\text{C}$ and (b) $T_g + 15^\circ\text{C}$

The results obtained are of prime interest from a fundamental point of view in order to better understand the complex physical behaviors of PLA. Moreover all these results constitute a valuable feedback for the elaboration of tunable PLA/nanocomposites

To conclude, the allocated beamtime has provided precious information regarding the structural evolution of PLA nanocomposites. Moreover, it has allowed us to test a homemade stretching device which has revealed to be perfectly adequate for our scientific approach.

Communication of the obtained results

International conference:

- G. Stoclet, J.-M. Lefebvre, R. Séguéla
 “In situ WAXS Characterization of the Strain-Induced Structural Evolution of Poly(D,L-Lactide) based nanocomposites”
 Material Research Society Fall Meeting, Boston, December 2010
- G. STOCLET, R. SEGUELA, J.-M. LEFBVRE, C. ROCHAS (Invited conference)
 “In situ WAXS and ex situ DSC characterization of the strain-induced structural evolution of poly(D,L-lactide) under tensile drawing”.
 4th Conference on Polymer Behavior - IUPAC; 20-23 Septembre 2010, Lodz (Poland)

- G. Stoclet, R. Seguela, J.-M. Lefebvre, C. Rochas (publicated conference)
« Caractérisation par WAXS in situ et DSC ex situ de l'évolution structurale d'un poly(D,L-lactide) induite par étirage »
MATERIAUX 2010, 18-22 Octobre Nantes

Publications:

- G. Stoclet, S. Barrau, R. Séguéla, J. Pérez, C. Rochas.
“Strain-induced structural evolution of Poly(D-L lactide)/ Carbon nanotubes nanocomposites : A WAXS/USAXS study”
In preparation
- G. Stoclet , R. Séguéla , S. Barrau , C. Rochas
”Direct evidence of the nucleating effect of clay platelets on the crystallization behaviour of Poly(lactic acid)”
To be submitted soon to Macromolecules
- G. Stoclet, R. Séguéla, J.M. Lefebvre, S. Li , M. Vert
“Structural evolution of polylactides upon stretching: Influence of the stereo-isomer content”
Submitted to Macromolecules