| ESRF | **In-situ study of the strain-induced structural evolution of Poly(lactic acid) stereocomplexes** | **Experiment number**: 02-01 827 |
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| **Shifts:** 9 | **Local contact(s)**: Cyrille Rochas | *Received at ESRF:* |

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**Report:**

In this study we have recorded both WAXS et SAXS patterns during uni-axial stretching of stereocomplexable PDLLA 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 a part of the results obtained, as some complementary experiments are still in progress.

**Background:**

Particular interest is growing towards polymers issued from renewable resources. Among these materials, Poly[lactic-acid] (PLA), which is a biodegradable polymer, seems to be one of the most promising candidates for the substitution of polyolefins. Depending on the synthesis route used, PLA homopolymers (i.e. PLLA and PDLA) or random or block copolymers can be obtained. Lots of research efforts have been paid to studying and understanding the strain-induced structural of PLLA homopolymers and PDLLA random copolymers. Besides it has been shown that :

- A strain-induced crystallization phenomenon occurs upon uni- and bi-axial stretching in the case of initially amorphous PLLA or PDLLA random copolymers.
- Initially semi-crystalline materials are stretchable and that several complex deformation mechanisms are involved.
- The crystalline form induced is the defective alpha form (i.e. the $\alpha$' form)

In the meantime a growing interest has been paid to studying blends of the two PLLA and PDLA pure homopolymers. This arises from the fact that, for such blends, a particular

crystalline form can be induced to know the stereocomplex crystalline form (sc form). Even if the thermally induced crystallization of these materials has been largely studied, there are actually no data about the strain-induced crystallization process for these materials. Also, few data are available regarding mechanical behavior of these materials.

Consequently this study is aimed at characterizing the structural evolution of PLLA/PDLA blends upon uniaxial stretching. Both WAXS and SAXS experiments have been performed in order to get access to a multi-scale characterization. Particularly both the influence of the drawing conditions (drawing temperature and strecthing speed) and the influence of the intial crystallinity of the material have been analyzed. Moreover the influence of the composition of the blends have been studied. Besides a racemic blend, denoted PLA50, that contains 50%wt of PLLA and 30%wt of PDLA and a blend containing 70%wt of PLLA (denoted PLA70) and 30%wt of PDLA have been studied.

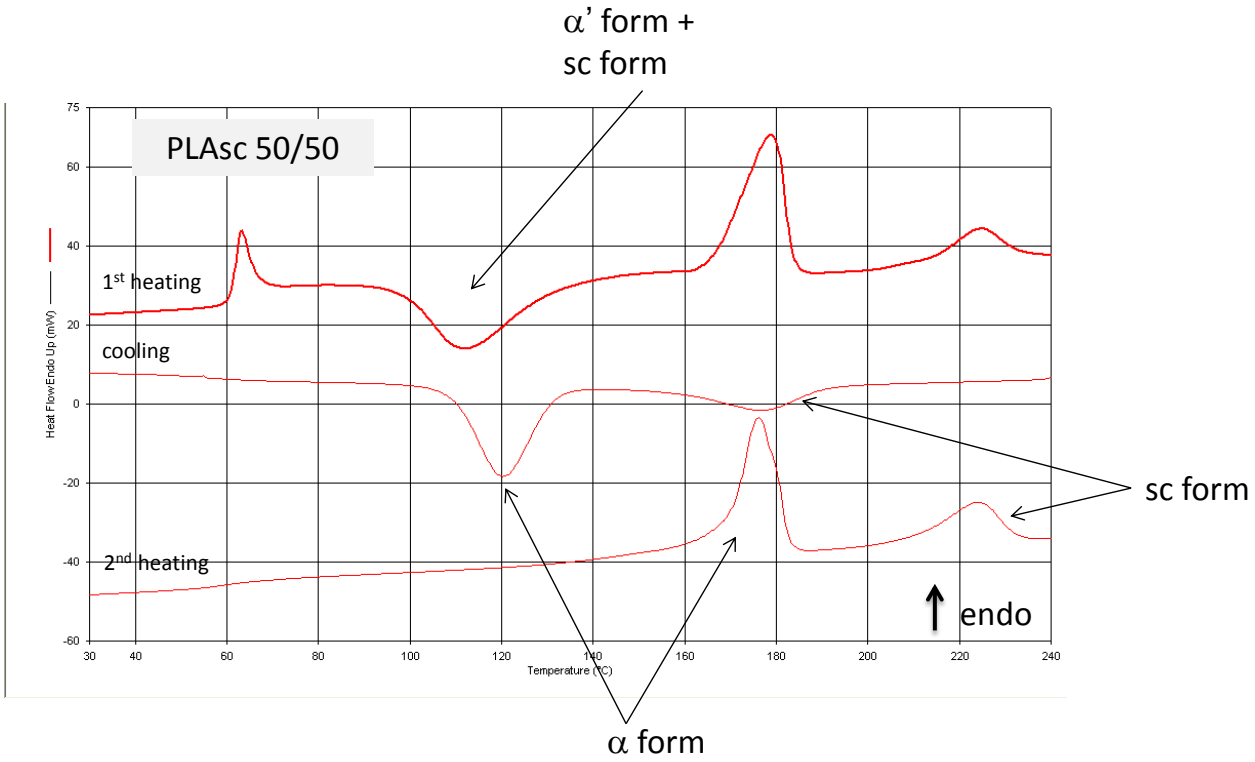
**Materials elaboration**

Blends were obtained by dissolution of the corresponding quantities of PLLA and PDLA into chloroform. The solution , vigorously stirred during 2 hours, was then cast onto teflon films. After drying under vaccum during 12h, about 1mm sheets were obtained by compression moulding at 250°C before quenching.

**Results**

The first part of the experiments have been focused on the characterization of the structural evolution of the materials upon heating. Indeed it is starting from these results that the drawing temperatures have been determined. Figure 1.a depicts the DSC thermograms recorded on the as elaborated PLA50 sample. On the first heating, a Cp drop charateristic of the glass transition is observed around 62°C. Then an exotherm characteristic of a cold-crystallization process occurs between 100°C and 140°C. Thanks to the WAXS patterns it has been determined that both the defective $\alpha$' form and the stereocomplex crystalline form (sc form) are induced during cold-crystallization. Finally, at higher temperatures, two endothermic peaks are observed. The first one, around 180°C is characteristic of the melting of the $\alpha$' crystals while the other one around 225°C is characteristic to the melting of the PLAsc crystals.
Using a deconvolution method previously used in a former study, the total crystallinity was calculated equal to 50% for both PLA50 and PLA70. In addition the respective crystals contents regarding the a' sc forms were found equal to 30% and 20% for PLA50 and 37% and 13% for PLA70 respectively.

(a)




(b)

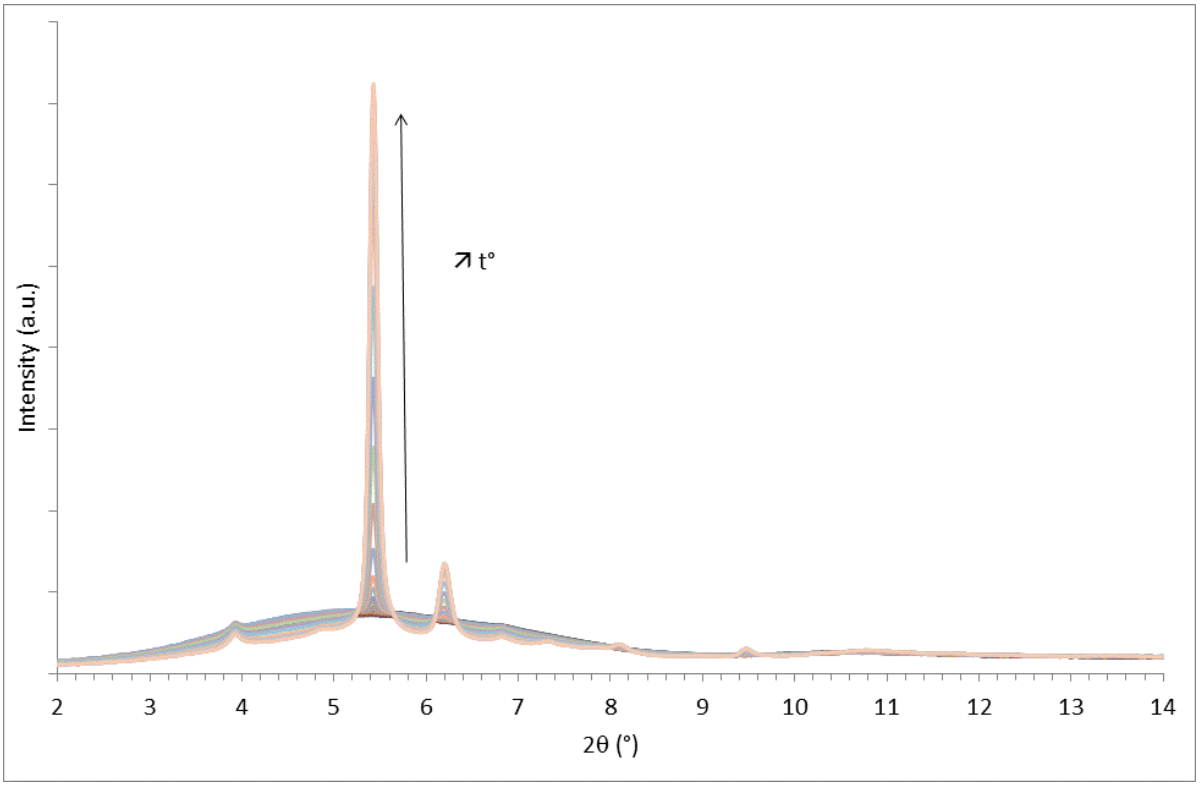
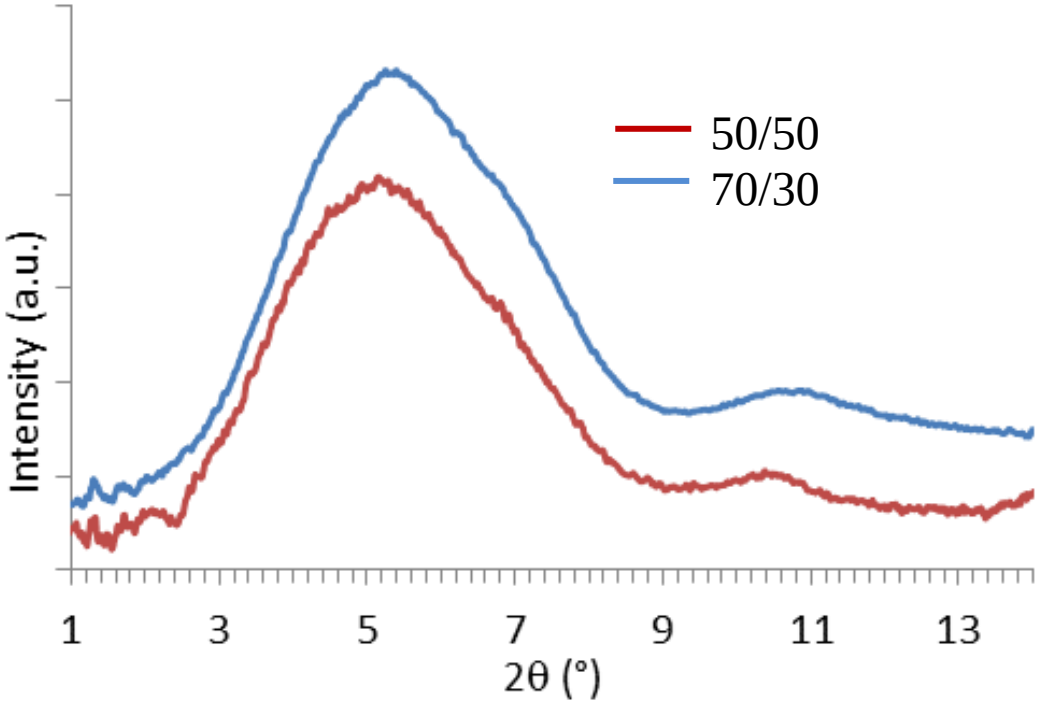



Figure1 : (a) DSC thermograms recorded on PLA50 and (b) evolution of the WAXS intensity profiles recorded in situ upon heating until 140°C.

Starting from these results three drawing temperature ranges were determined.

The main part of the study was to characterize the structural evolution of the materials upon uni-axial stretching. As illustrated by the integrated intensity profiles of the as elaborated materials depicted on figure 2a, the two blends are initially amorphous.

(a)




(b)

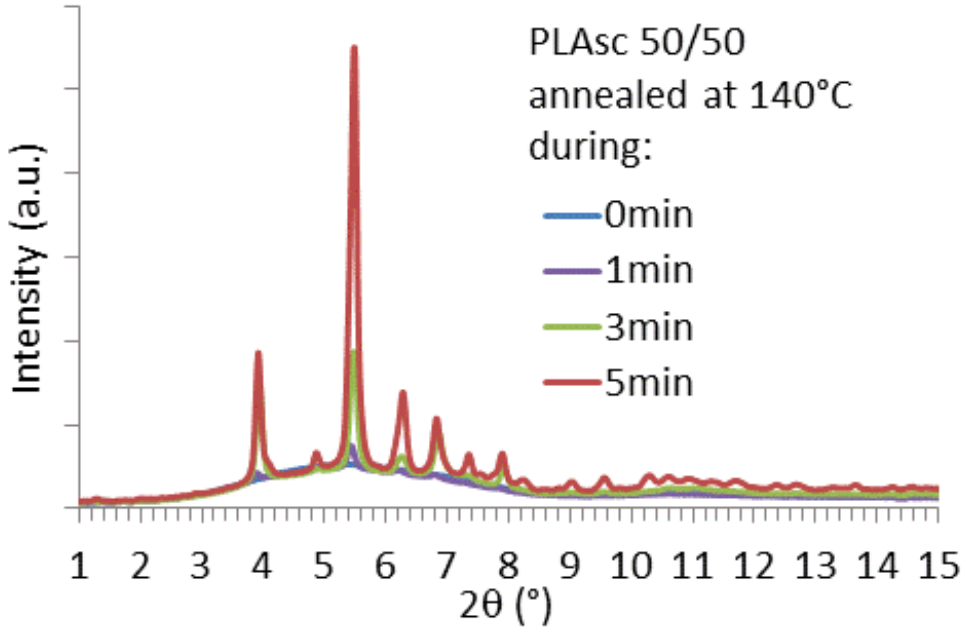
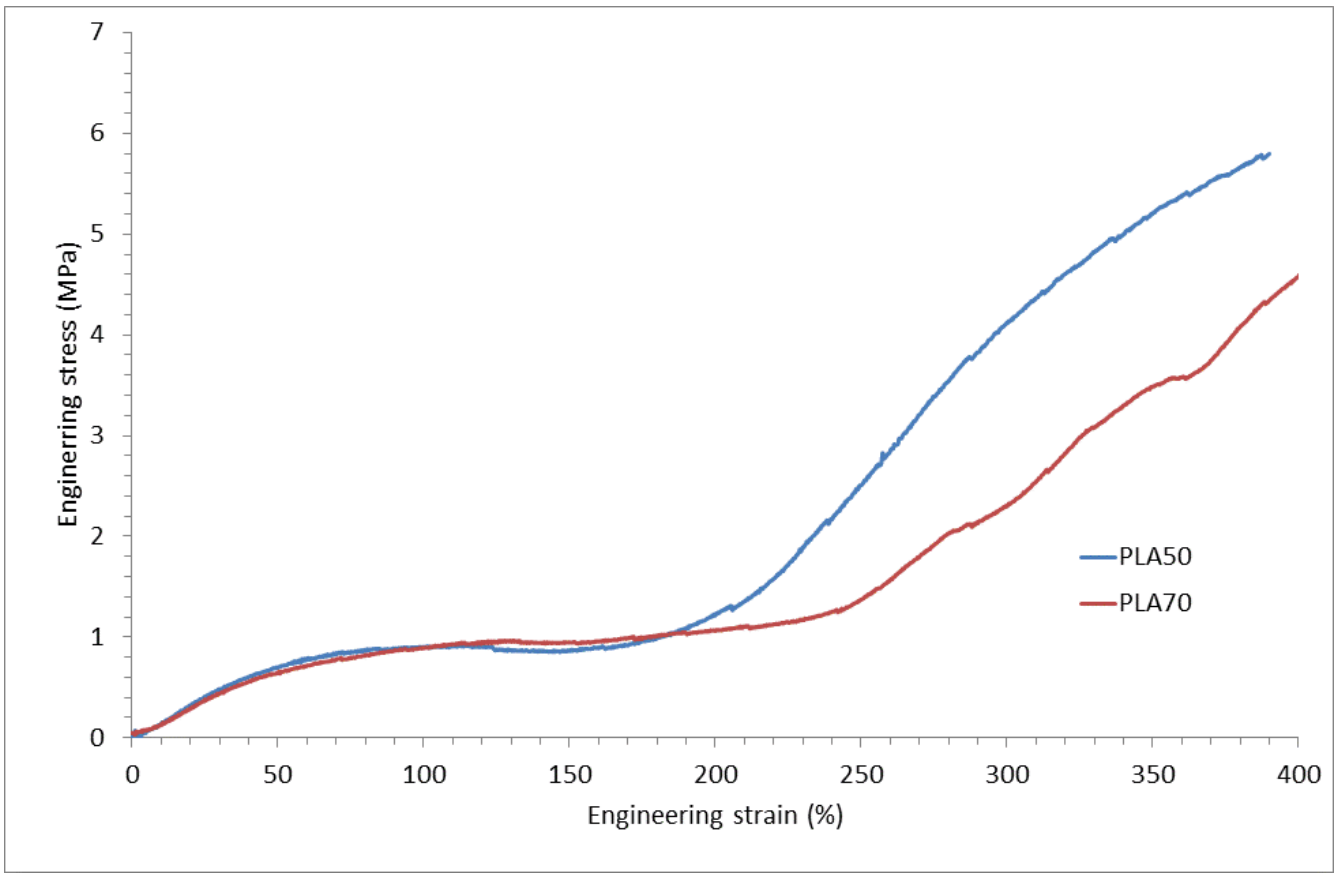



Fig 2: (a) Integrated intensity profiles of the as elaborated PLA50 & PLA70 samples and (b) integrated intensity profiles of the PLA50 samples annealed at 140°C during different times.

In order to investigate the effect of the initial crystallinity, PLA50 and PLA70 samples were annealed at 140°C during different times in order to get samples having crystallinity ratios varying from 0% to 50%.

The first draw temperatures range investigated was the [60°C-80°C] one, i.e. above Tg but below the cold-crystallization. Engineering stress-strain curves obtained for PLA50 and PLA70 respectively drawn at Td = 70°C are reported in figure 3a. The mechanical behavior observed is similar to the one previously reported in the case of the PLLA homopolymer. Particularly a strain hardening phenomenon occurs for draw ratios above 200%. Worth noticing is that the strain hardening process, ascribed to a strain-induced crystallization in the case of PLLA homopolymer, starts slightly later for PLA70.
From a structural point of view, on figure 3b are reported the integrated intenisty profiles computed from the WAXS patterns recorded during drawing of initially amorphous PLA50 drawn at Td = 70°C. As can be seen, diffraction peaks can be observed when the draw ratio increases. Moreover it appears that only the α' crystalline form that is induced upon drawing.

(a)




(b)

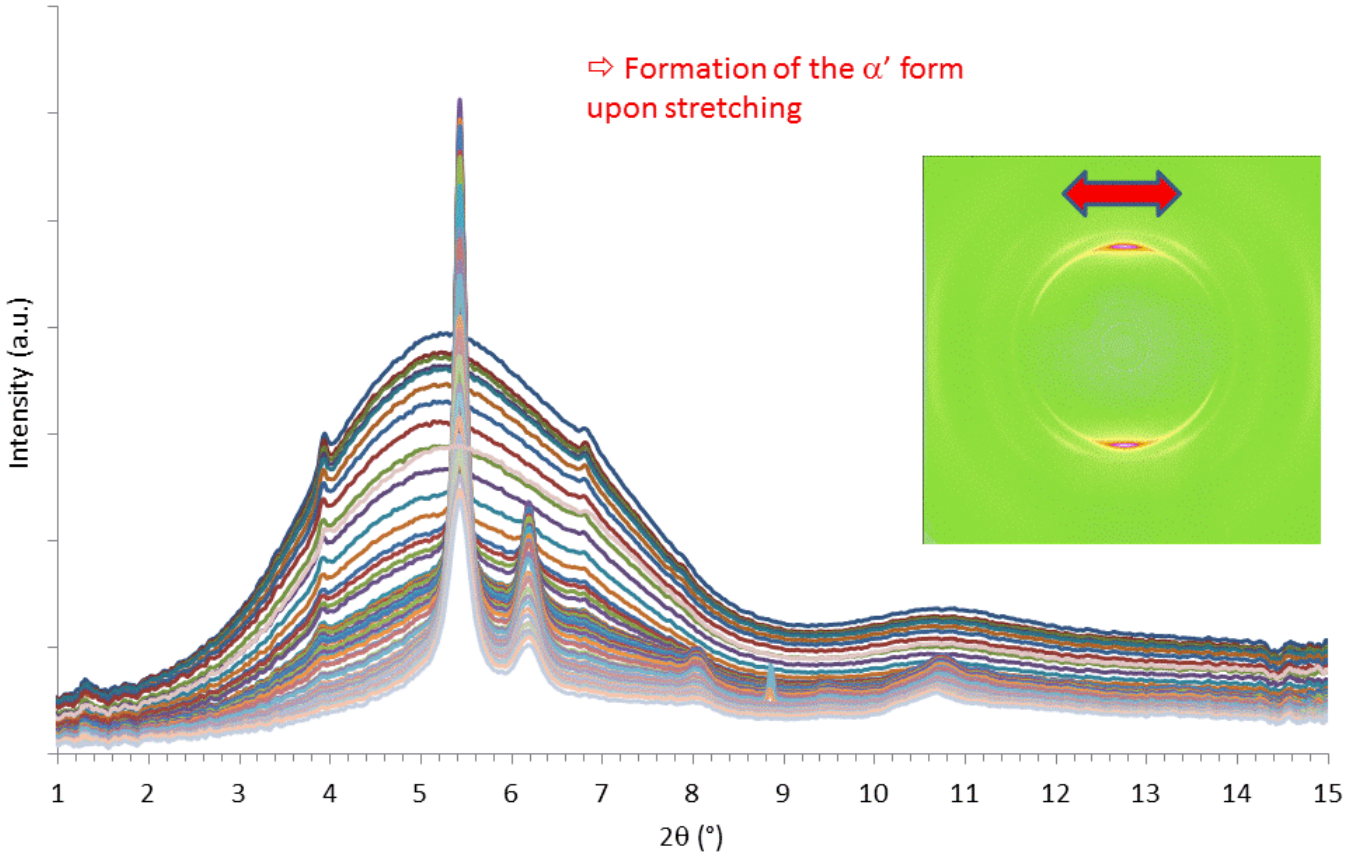



Figure 3 : (a) Engineering stress-strain curves of PLA50 and PLA70 drawn at Td = 70°C & (b) Integrated intensity profiles computed from the WAXS patterns recorded on the PLA50 sample drawn at 70°C. (The WAXS pattern depicted corresponds to a draw ratio of 200%)

The maximum crystallinity achieved at the end of drawing was calculated equal to 30%. Such a crystallinity ratio is of the same order of magnitude than the one reported in the case of pure PLLA. Moreover the crystallinity ratio achieved at the end of drawing is the same for PLA50 and PLA70. This demonstrates that both PLLA and PDLA forms α' crystals.
Moreover WAXS pattern reported on figure 3, that was took at e = 300%, indicates the strain-induced crystals are oriented along the draw direction.
The calculation of the evolution of crystallinity as a function of the deformation for both PLA50 and PLA70 indicates that the strain-induced crystallization process starts slightly later in the case of PLA70. This is in good agreement with the mechanical behaviors previously discussed and in also indicates that the strain hardening phenomenon corresponds to the formation of α' crystals in both cases.

SAXS results obtained for the same draw conditions are reported in figure 4.

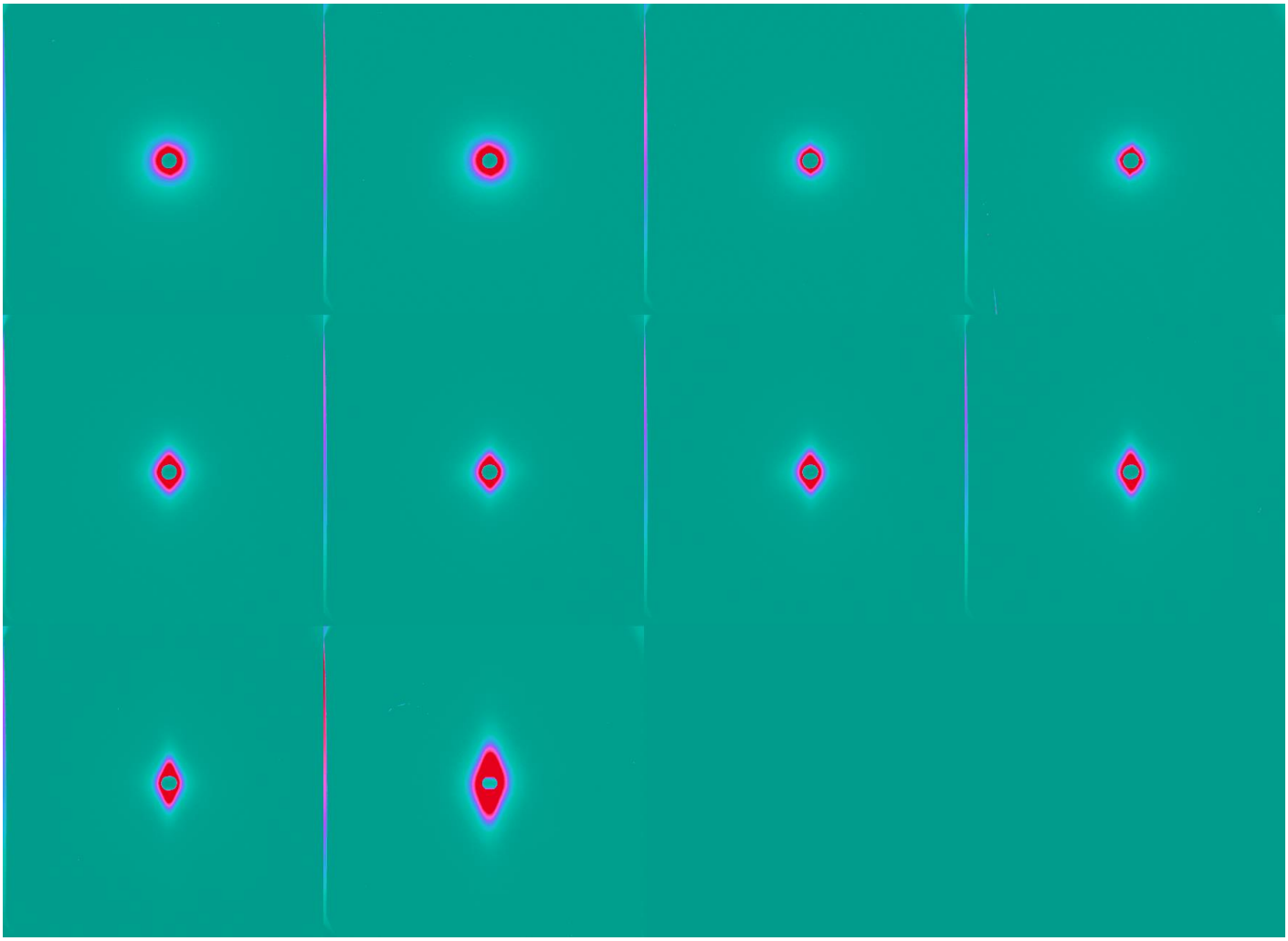


Figure 4: SAXS patterns recorded at different draw ratios on PLA50 drawn at Td = 70°C (the draw axis is horizontal)

SAXS patterns indicate that the strain-induced crystallization process is accompanied by a fibrillation phenomenon as previously reported in the case of the homopolymer. The kinetics of the fibrillation process as well as the precise characterization of the fibrillar structure is still in progress.

Regarding the influence of the initial crystallinity in the same draw temperatures ranges, results clearly show that the presence of sc crystals induce a fragilization of the material. Indeed while initially semi-crystalline α PLA can reach large plastic deformation ratios, no significant deformation at break have been observed when sc crystal contents as low as 5% were present.

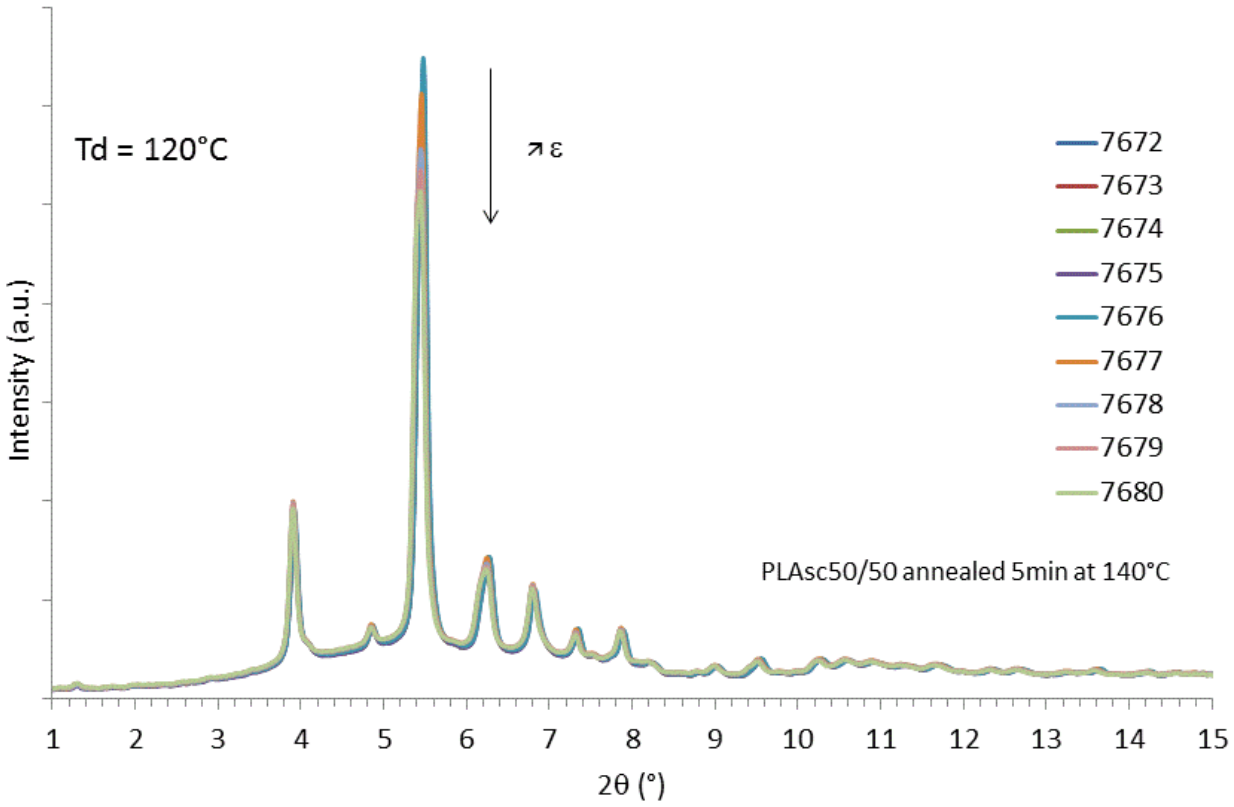



Fig 5: Integrated intensity profiles computed from the WAXS patterns recorded on a initially semi-crystalline PLA50 sample drawn at Td = 120°C.

In a previous study, we proposed a model describing the plastic deformation mechanisms involved during the deformation of initially semi-crystalline PLA. Besides, we shown that the shearing mechanism governs the deformation of the materials at the beginning of stretching. Thus, it can be assume that the non-deformability of the blends arises from the fact that shearing of the PLAsc crystals is not possible for these drawing conditions. This can arises from the fact that hydrogens bonds ensure a strong inter-chains cohesion in the sc crystals.

The second draw temperature range investigated was the [140°C-150°C] one, that's to say above the cold-crystallization but below the melting of the α' crystals. As the cold-crystallization occurs quicly, only samples having a high crystallinity content have been stretched. Moreover as during the cold-crystallization a part of sc crystals is induced. Thus the same behavior than the one obtained for lower Td in the case of initially semi-crystalline samples with sc crystals, i.e. a brittle behavhior, was observed.

Finally drawing experiments above 190°C, i.e. above the melting of the α' crystals, were carried out. At these temperatures only sc crystals are present into the materials.As can be seen on the engineering stress-strain curves recorded for PLA50 at 190°C reported in figure 6, there's no significant plastic deformation of the sample. The same kind of results were obtained for PLA70.

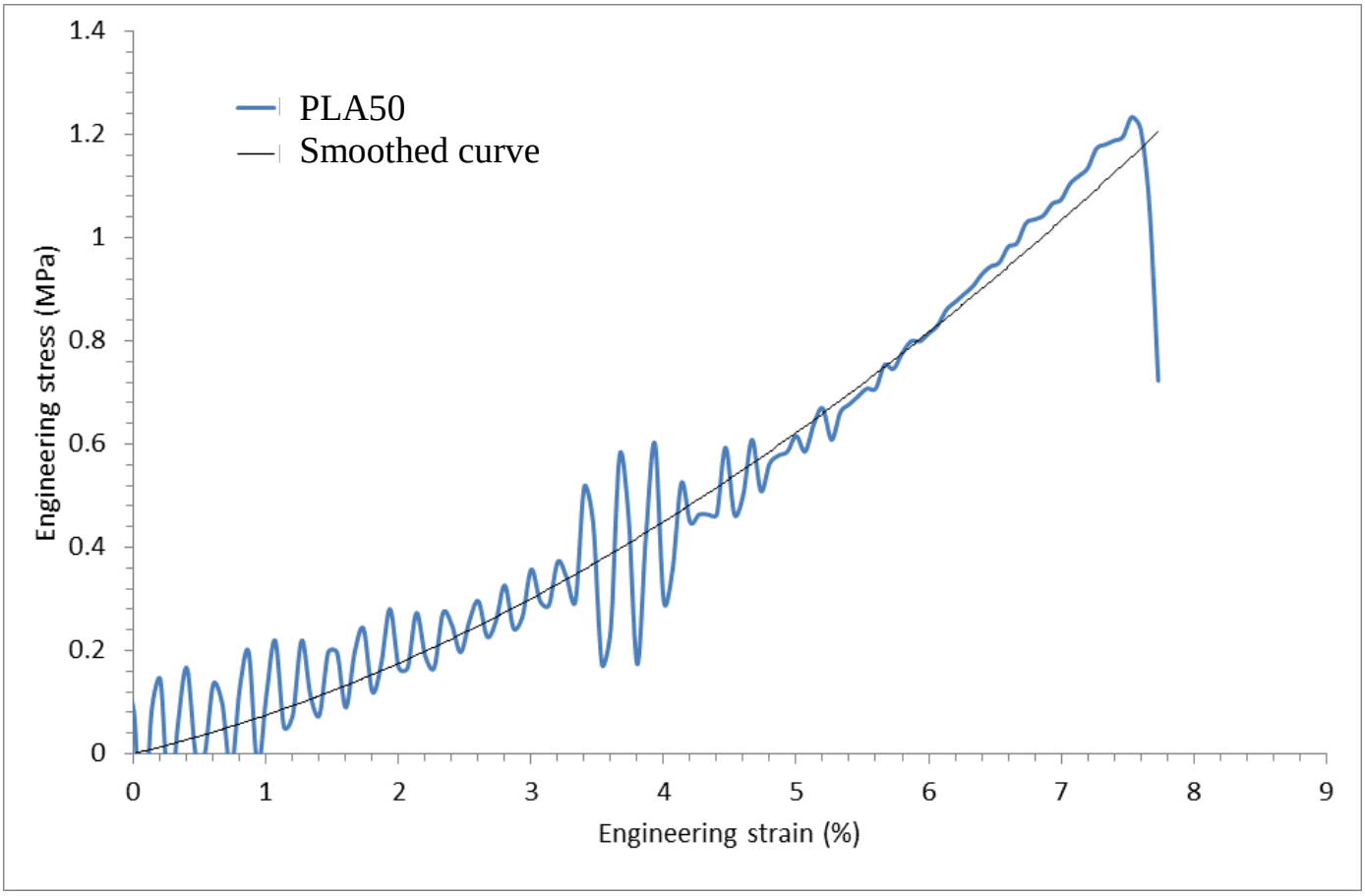



Figure 6 : Engineering stress-strain curve of PLA50 drawn at Td = 190°C

## Conclusion

SAXS and WAXS experiments have allow first to characterize the structural evolution of PLA50 and PLA70 blends upon heating in order to determine the drawing conditions to investigate. Besides it has been shown that during the cold-crystallization phenomenon occuring upon heating, both the α' and the sc crystalline forms are induced.

One of the main result of this study is that the presence of sc crystals induce a britlle character of the material. This result is of prime interest from both scientifical and industrial point of view and the origin of the latter has to be more deeply investigated. Neverthelless it can be reasonabbly assume that this fragility arises from the fact that the shearing mechanism previously reported in the case of the homopolymer is can not be activated in the case of the stereocomplexable blends, probably dut to the presence of the hydrogens bonds between the macromolecular chains in the sc crystals. Complementary experiments including compression tests and molecular dynamics are still in progress.

Also this study has allow to show that it is the regular a' crystalline form, that is encoutered upon drawing of pure homopolymers or random copolymers, that is induced upon stretching in the case of initially amorphous blends. This may indicates that, from an energetical point of view, this crystalline form is easier to form upon stretching.

Finally, regarding the influence of the initial composition on the structural evolution, results have shown that :

- Whatever the composition and the drawing conditions, no stereocomplex crystal can strain-induced.
- The amount of a' crystal induced upon stretching don't significantly depend of the initial composition.

## Note

Due to technical problems with the monochromator during the energy change form SAXS to WAXS, 1 shift ½ has been lost.
SAXS results are not yet fully analyzed as there were some problems with the treatments of the patterns that has involved a re-treatment process. Consequently an additional experiment report will be published in a near future.

## Communication of the obtained results :

Results will be presented through an oral communication at the MRS2013 Fall Meeting

Publications :

Stoclet G., Lefebvre J.-M., Séguéla R.
*In preparation*
Time-resolved characterization of the strain-induced molecular ordering of PLLA-PDLA blends upon stretching.