| ESRF | **Experiment title: Origin of the brittle to ductile transition induced by biaxial stretching of amorphous polymers : case of Polylactic acid** | **Experiment number**: 02-01 895 |
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| **Beamline**: D2AM | **Date of experiment**: from: 16th November 2018 to: 19th November 2018 | **Date of report**: Jan 2020 |
| **Shifts: 9** | **Local contact(s)**: Isabelle Morfin / Gilbert Chahine | *Received at ESRF:* |

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**Report:**

Some studies showed, in the case of Polylactide (PLA), that a brittle to ductile transition (B-D transition) can be induced thanks to appropriate thermomechanical treatments. As the brittleness of PLA is one of its main drawbacks, understanding this behavior is of prime interest. The origin of this transition, in the case of PLA, was ascribed to the formation of an ordered phase during stretching[i]. However, a similar transition is observed in the case of polystyrene (PS) even if this polymer remains amorphous. The goal of this work thus lies in a better understanding of the B-D transition for bi-oriented PLA films. The role of strain-induced phases as well as the chain orientation in the ductility improvement will be investigated. Thus, two PLA grades, a crystallizable and a non crystallizable one, will be compared in order to separate the respective effects of crystalline structure and macromolecular orientation on the mechanical behavior.

**Objectives:**

Particularly, the main goal of this study was to accurately determine the relationships between the macromolecular orientation degree and the plastic deformation mechanisms involved during cold drawing of initially amorphous Polylactide, and more generally of initially amorphous polymers. Particularly it consisted in studying parameters such as crazing density, crazes sizes, kinetics of developments, as a function of the initial macromolecular orientation.

Another goal of this work was to assess the influence of the presence of an initially ordered phase on this behavior. Indeed, ordered structures such as crystals or mesomorphic phases, can be induced upon biaxial stretching and it is of prime interest to know if and how they influence the brittle to ductile transition. Thanks to these data it would be thus possible to get information about the structural origin of the crazing to shear banding transition responsible of the stretchability enhancement of PLA. In addition, tests will be also carried out on biaxially stretched PS in order to assess if the origin determined on PLA is the same in the case of PS and thus can be transpose to amorphous polymers.

## Experimental :

In situ simultaneous SAXS/WAXS experiments during uniaxial stretching at room temperature were carried out on as cast PLA and PLA films biaxially drawn according to different conditions. Particularly, in order to separate the effects of crystallinity from the ones of macromolecular orientation, two types of PLA were tested to know:

- C-PLA which is a grade able to crystallize.
- NC-PLA which is a grade unable to crystallize.

In the same way, films of PS have been also tested.

## Results :

The mechanical tests carried out, depicted in Figure 1, indicate that the unstretched (isotropic) samples are very brittle, while a ductile behavior is observed for the C-PLA samples as soon as the biaxial draw ratio is above 2x2. Similar evolution is observed for NC-PLA except that the transition occurs for a slightly higher critical draw ratio, i.e. 2.5x2.5. These results confirm the thermomechanically induced B- D transition in both PLAs.

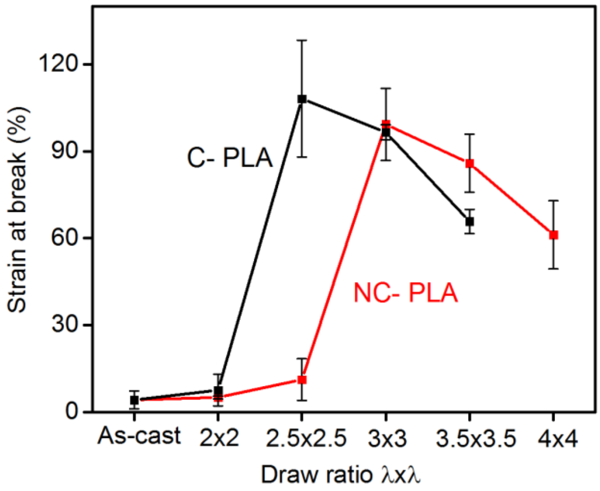


Figure 1: Strain at break of as cast and BO films of two grades of PLA uniaxially drawn at room temperature as a function of draw ratios.

Regarding the origin of this B-D transition, results obtained by means of SAXS and depicted in Figure 2, clearly show that it originates from a transition from crazing to shear banding.

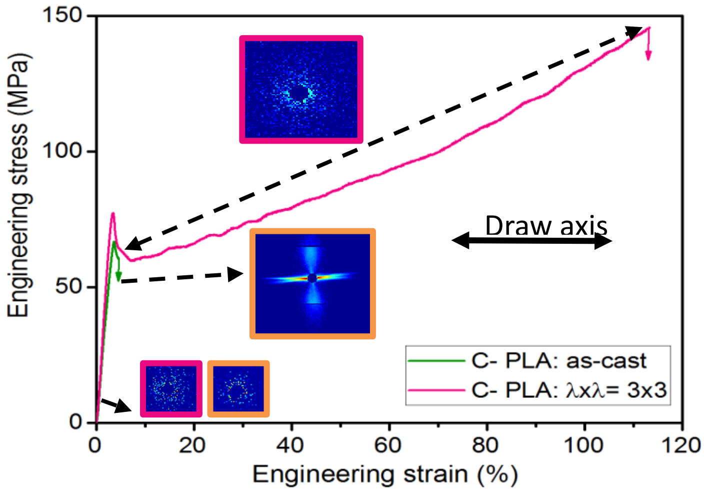

Figure 2: SAXS patterns recorded before sample break of as- cast C- PLA and a typical pattern obtained during entire uniaxial stretching of a C- PLA biaxially stretched at 3x3.

In order to go further in the understanding of this plastic deformation mechanisms transition, PLA samples biaxially drawn at intermediate ratios have been analyzed. An example of SAXS results obtained is depicted in Figure 3.

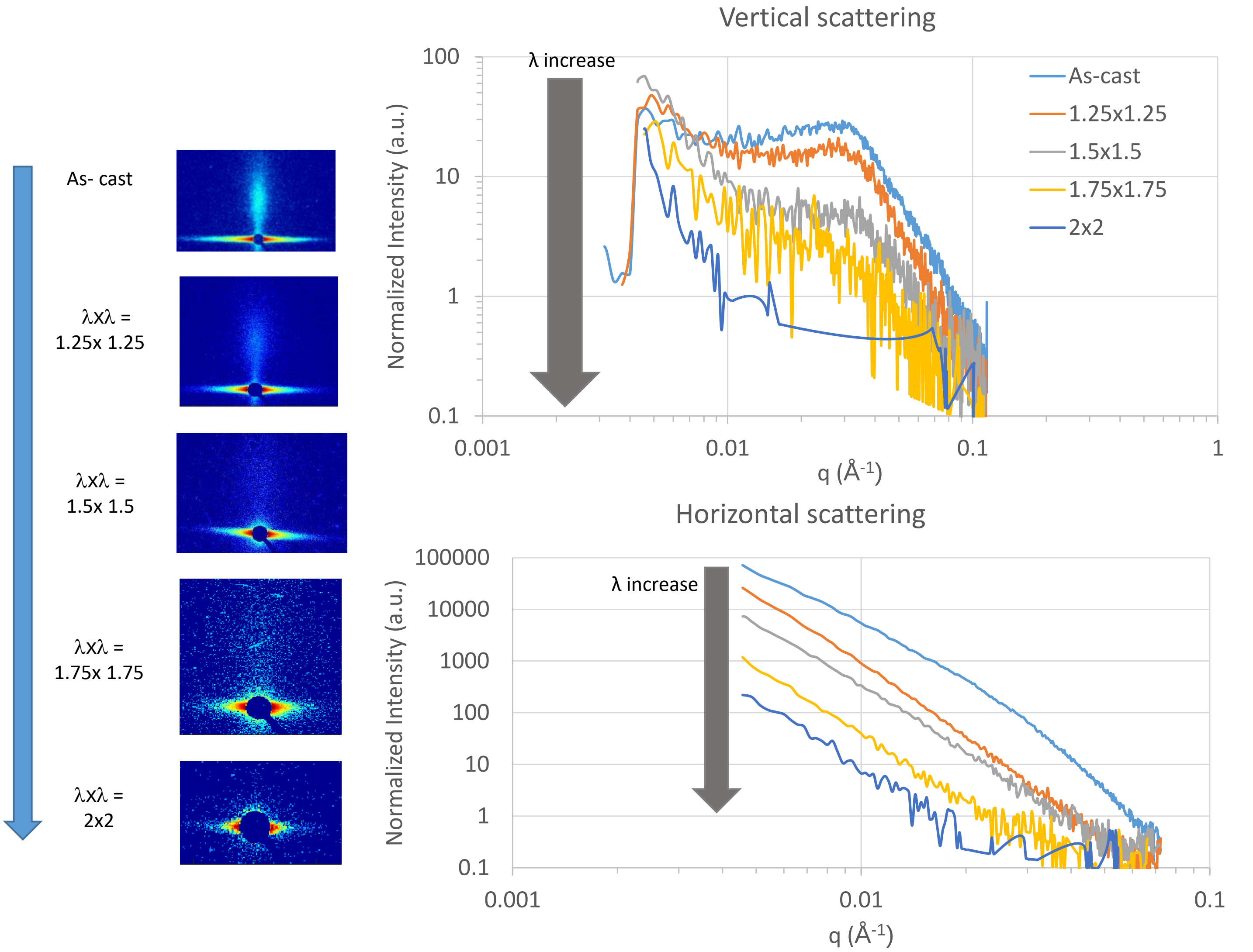


Figure 3: SAXS patterns obtained during uniaxial stretching of PLA samples biaxially oriented at different ratios and evolution of the scattered intensity along the vertical and horizontal directions.

A quantitative analysis of the results revealed that the increase of the biaxial stretching ration, i.e. of the macromolecular orientation, involves a decrease of the crazing density while the geometry of the craze (i.e. fibrils diameter and mean distance between fibrils) remains unchanged.
This result is of prime interest to understand the origin the crazing to shear banding transition. Indeed, complementary experiments allowed us to determine that the origin of the crazing to shear banding transition is due to the fact that macromolecular orientation involves an increase of the critical nucleation stress of crazing which, the increase of elongation, became higher than the critical stress for activation of shear banding.

## Conclusions :

Thanks to the results obtained we demonstrate that :

- The brittle to ductile transition observed in the case of PLA doesn't originate from the formation of a crystalline phase but only originates from macromolecular orientation aspects.
- This B-D transition corresponds, in fact, to a transition of the plastic deformation mechanisms involved (from crazing to shear banding).

⇨ A paper has been submitted to *Polymer* (revised version under review)

- A similar trend has been observed in the case of PS tending to show the universal character of the behavior observed.
- The effect of macromolecular orientation of the plastic deformation mechanisms has been clearly assessed and explain

## References :

[i] Jariyasakoolroj, P., Tashiro, K., Wang, H., Yamamoto, H., Chinsirikul, W., Kerddonfag, N., & Chirachanchai, S. (2015). Isotropically small crystalline lamellae induced by high biaxial-stretching rate as a key microstructure for super-tough polylactide film. Polymer, 68, 234-245.