



	Experiment title: In-situ study of the strain-induced structure evolution of a new polyester issued from renewable resources: The Poly(Ethylene Furanoate)	Experiment number: MA-3034
Beamline: ID02	Date of experiment: from: 17 th May 2016 to: 19 th May 2016	Date of report: Jan 2020
Shifts: 6	Local contact(s): Peter Boesecke	<i>Received at ESRF:</i>
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Report:

Among “green” alternatives for oil-based commodity plastics like Polyethylene, Polyamides, and Poly(-Ethylene Terephthalate) (PET), a new class of polyesters synthesized from furanedicarboxylic acids (FDCAs) is currently in the spotlight of both the academic and industrial communities. Of particular interest is Poly(Ethylene-2,5-Furanoate) (PEF), which can be synthesized from biobased monomers. Owing to its physical properties, PEF qualifies as a strong candidate for PET substitution particularly in bottle, fiber and film packaging applications. In the present study the structural evolution of PEF upon uniaxial stretching has been investigated by means of in-situ Wide Angle and Small Angle X-ray Scattering experiments.

In addition to this initial goal, the relationships between the crystalline structure and the thermal behavior of Poly(ethylene 2,5-furandicarboxylate) has been also assessed.

Experimental :

For studying these two topics, in situ simultaneous SAXS/WAXS experiments were carried out:

- during uniaxial stretching in the rubbery state to assess the strain induced structural evolution at different length scales. Regarding this part, both the effects of the stretching temperature and stretching speed have been studied.
- During thermal treatments such as cooling and heating to understand the complex thermal behavior observed during DSC experiments.

Results :

Structural evolution of PEF upon stretching

Figure 1 depicts the mechanical behavior of PEF upon uniaxial stretching as a function of the temperature. As can be seen the mechanical behavior observed strongly depends on the stretching with:

- A heterogeneous deformation for $T_d \leq 70^\circ\text{C}$ followed by a strain-hardening stage.
- A homogenous deformation for $75 \leq T_d \leq 85^\circ\text{C}$ with a presence of a strain-hardening stage at high deformations.
- A homogenous deformation for $T_d \geq 90^\circ\text{C}$ without any strain-hardening.

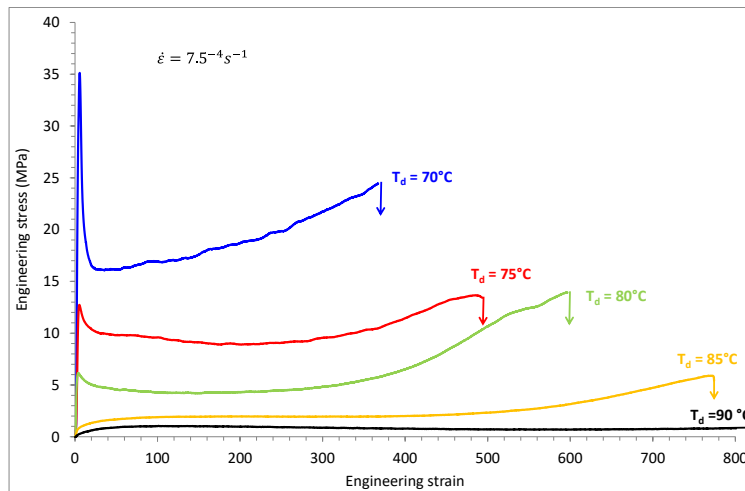


Figure 1: Mechanical behavior of PEF upon uniaxial stretching as a function of the stretching temperature.

This behavior is similar to the one observed for PET. Representative SAXS-WAXS patterns collected just before sample's breaking are depicted in Figure 2.

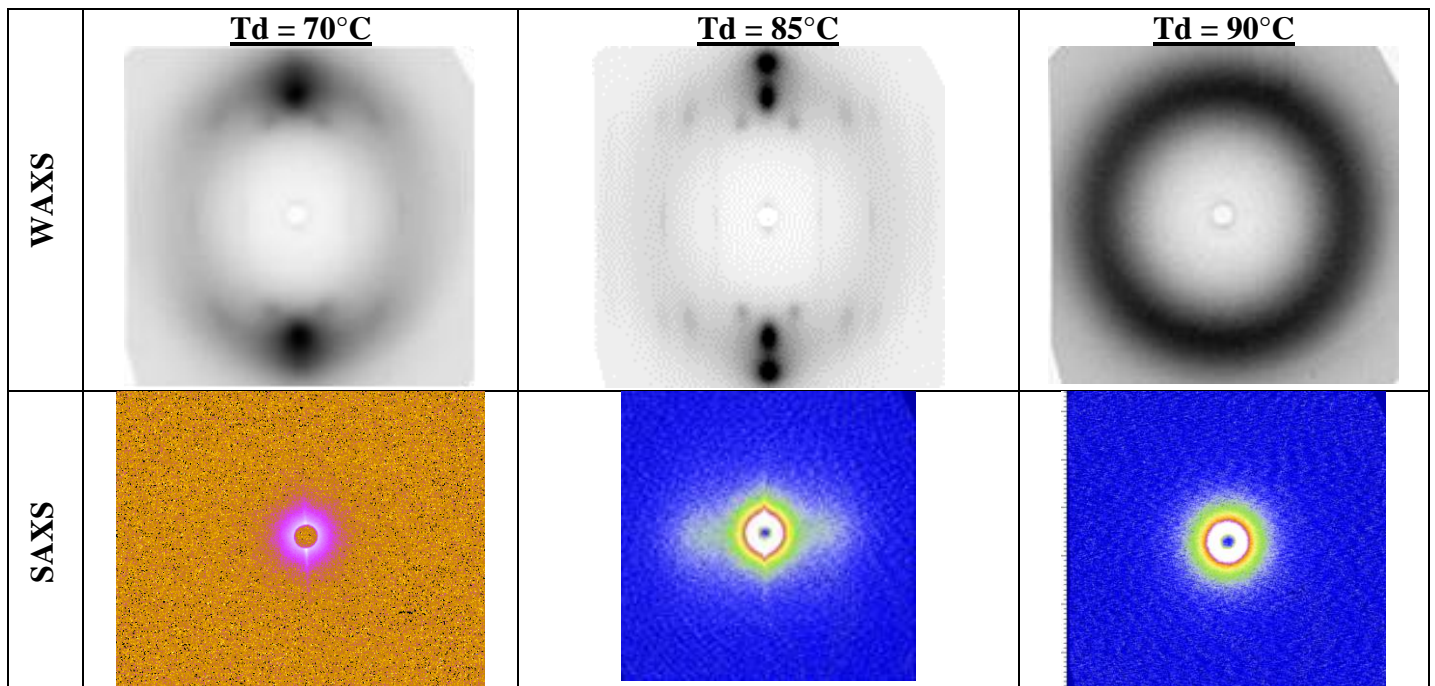


Figure 2: Representative SAXS-WAXS patterns recorded just before sample's break for different stretching temperatures.

Thereby the in-situ simultaneous SAXS-WAXS analyses allowed us to determine the role of both stretching speed and stretching temperature on: the nature of the strain-induced structure, the content of this phase, the macromolecular orientation degrees. In addition, a careful analysis of the data obtained on samples where a mesomorphic phase has been induced allowed us to propose a structural representation of this para-crystalline phase as depicted in figure 3.

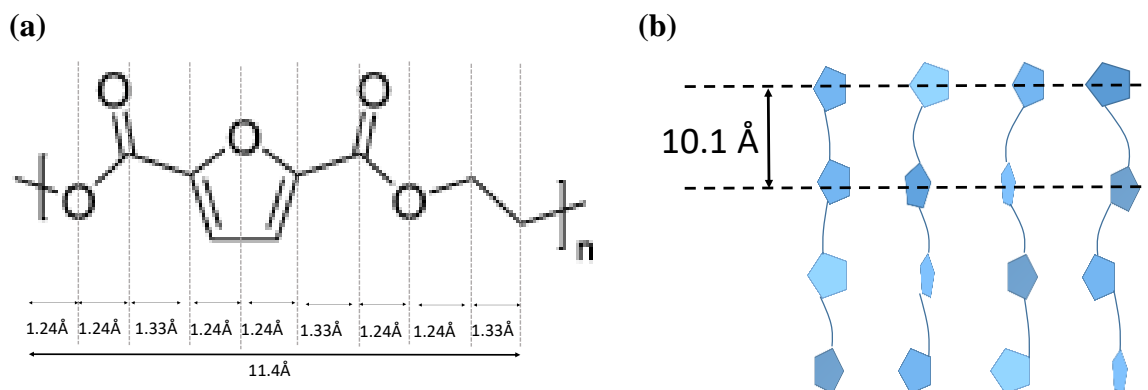


Figure 3: (a) representation of the PEF monomeric unit and (b) structural representation of the mesomorphic phase into PEF.

Relationships between the crystalline structure and the thermal behavior of PEF

A review of the literature shows that polymers may sometimes exhibit a complex thermal behavior. Our previous results indicated that PEF is one of those polymers as illustrated by Figure 4 where the DSC thermograms recorded upon heating after a crystallization from the melt at two different temperatures, i.e. 140°C and 190°C respectively, are reported.

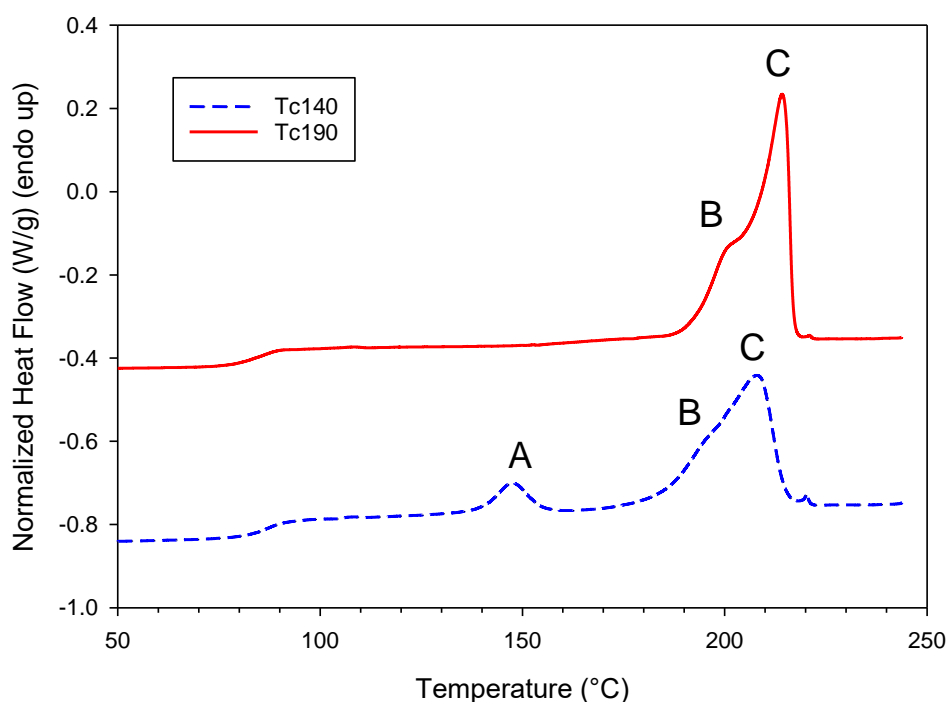


Figure 4: DSC thermograms recorded upon heating of PEF samples crystallized from the melt at 140°C (PEF-140) and 190°C (PEF-190) respectively

Besides, PEF exhibits:

- A multiple melting behavior around 200°C
- A small endotherm around 150°C ascribed to the melting of secondary crystals which are formed at low crystallization temperatures.

The multiple melting behavior of polymers has been largely studied in the past and several explanations have been proposed depending on the nature of the polymer, to know:

- The melting of crystals of different nature
- The melting of two different populations of crystals
- The occurrence of a melting - recrystallization - re-melting process.
- The occurrence of a phase transformation process.

On the other hand, the presence of secondary crystals into the polymer, characterized by the presence of a small endothermic peak at low temperatures is now well established. However, the structure and location of these secondary crystals remains debated.

Consequently, the goal of this work was i) to determine the origin of the multiple melting behavior observed in PEF and ii) to get new insights regarding the structure and location of secondary crystals.

The first set of experiments consisted in following by means of SAXS and WAXS the evolution of the structure of PEF-140 and PEF-190 upon heating.

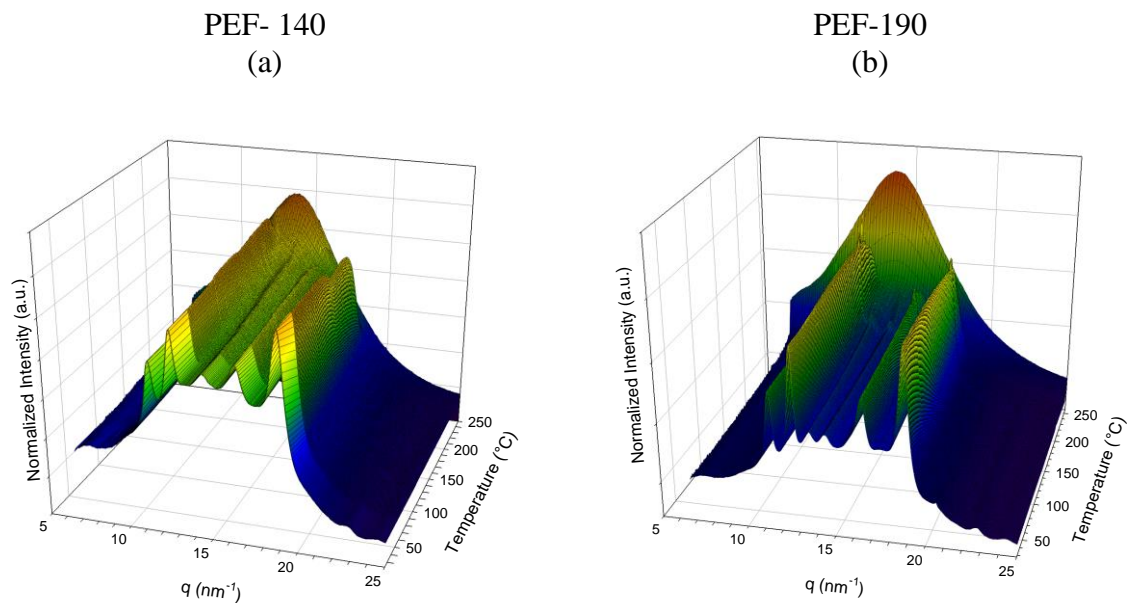


Figure 5: Evolution of the WAXS profiles recorded upon heating for two PEF samples crystallized from the melt at (a) 140°C and (b) 190°C

From these results it was possible to confirm that i) the small endothermic peak observed corresponds to a melting process and ii) that the multiple melting endotherm do not correspond to a phase transformation process. To go further, an in-depth analysis of the SAXS-WAXS data was carried out. Besides, the scattering invariant, the crystalline and amorphous lamellae thickness and the long period were calculated. Data are depicted in figure 6.

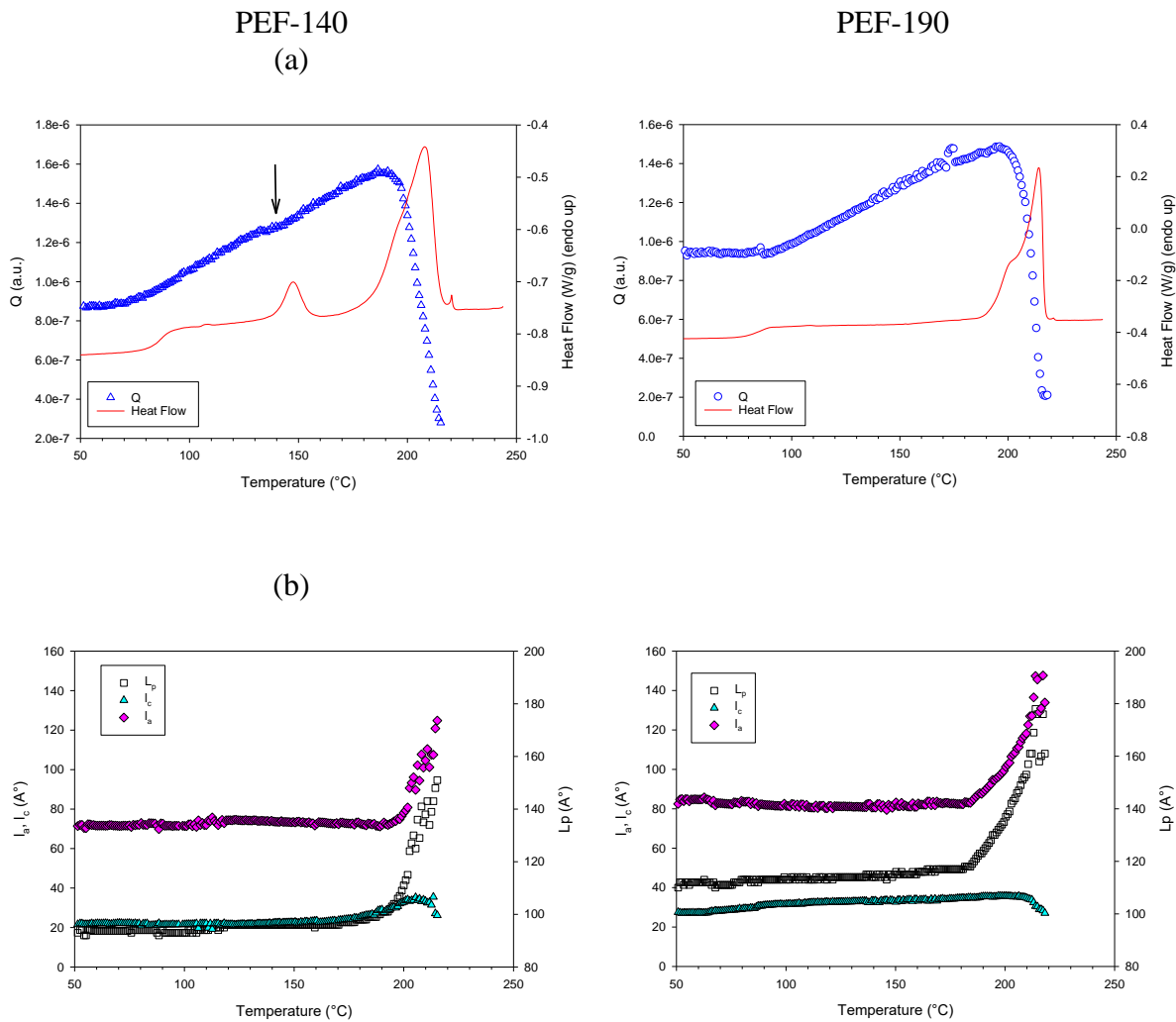


Figure 6: Evolution of (a) the scattering invariant (Q) and (b) the crystalline and amorphous lamellae thickness as a function of the temperature for PEF-140 (left column) and PEF-190 (right column)

From these data it has been possible to prove that the multiple melting phenomenon observed for PEF is due a melting – recrystallization –(re)melting process.

Finally, these data also allowed to get new insights regarding the structure and location of the secondary crystals which is depicted in Figure 7. According to this model, secondary crystals are located between the primary crystalline lamellae and consists in bundle like crystals rather than chain folded crystalline lamellae.

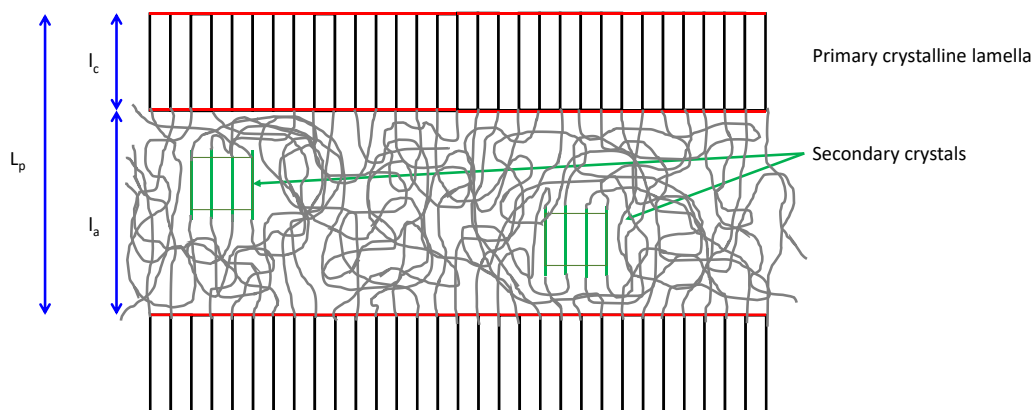


Figure 7: Schematic representation of the secondary crystals in PEF

In conclusion very interesting and promising results have been obtained thanks to those experiments. On the one hand the data collected during uniaxial stretching of PEF allowed to determine the relationships between the structural evolution and the mechanical behavior of PEF. This is of prime interest as PEF is a new emerging polymer and the optimization of its end to use properties is crucial in view of enlarging its application fields. On the other hand, the data obtained regarding the thermal behavior of PEF allowed to understand the complex behavior observed. In addition, thanks to these results, a new model regarding the secondary crystals in semi-crystalline polymers has been proposed.