



Assessment of PEF and PET stretch ability above T_g

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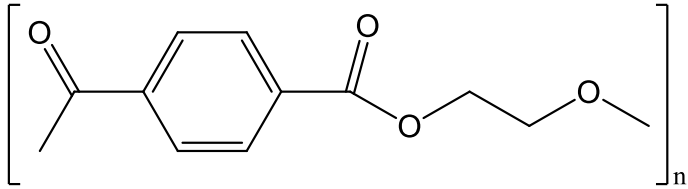
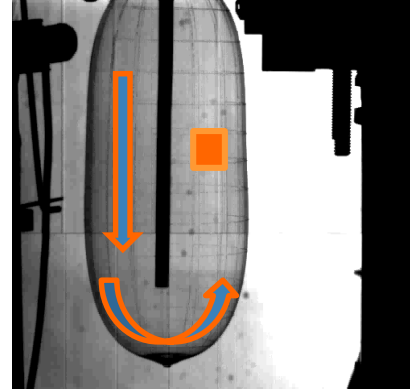
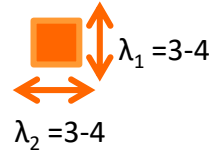


Bottles market

- ❖ Leader in this field until the 80's

- Poly(ethylene terephthalate)

- ❖ Bottles forming= reaching of high deformation above T_g



PET

- ❖ Good mechanical, thermal and barrier properties

- ❖ Transparency

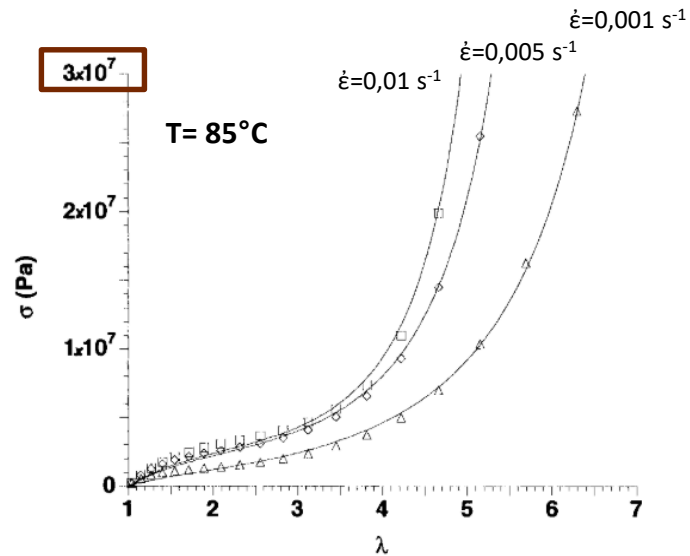
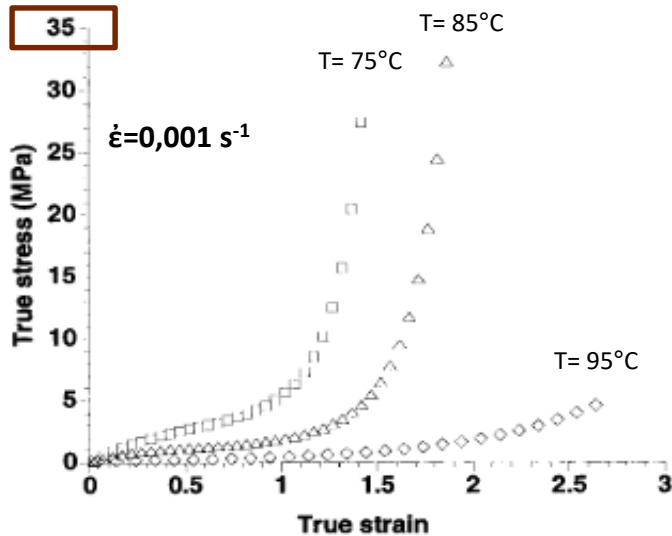


Around 20/30% of crystal

PET uniaxial stretching

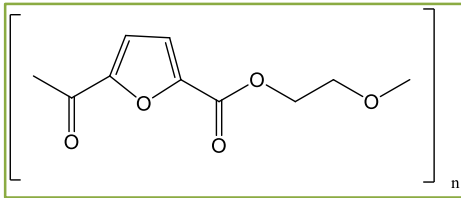
- ❖ From a certain deformation development of a strain hardening
- ❖ Apparition of a strain hardening = microstructural changes

$$\lambda = \exp(\varepsilon)$$



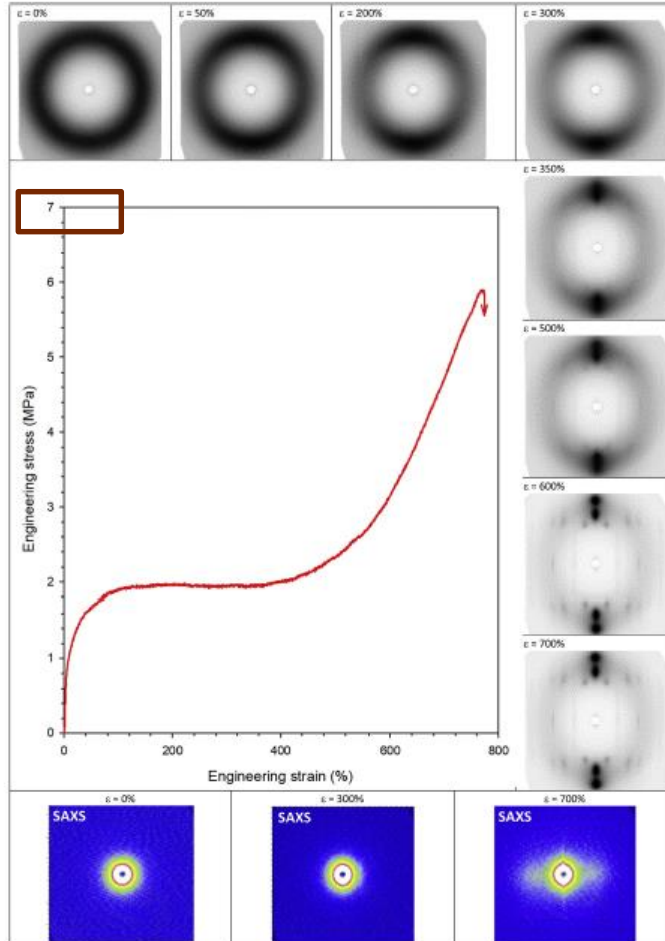
Natural Draw Ratio (NDR) \approx 2-3

PEF uniaxial stretching



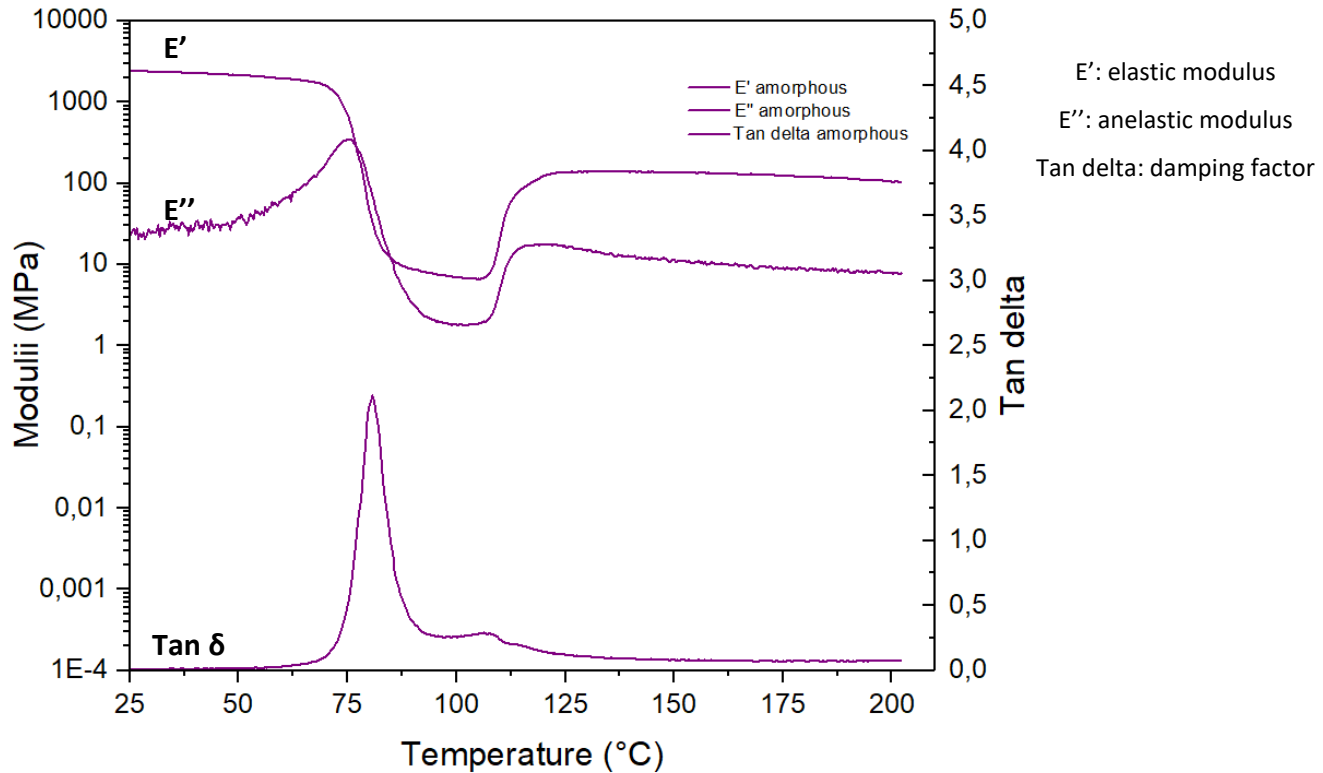
Poly(ethylene furandicarboxylate)

- ❖ PEF stretching at 85°C , $\dot{\epsilon}=7,5*10^{-4} \text{ s}^{-1}$
- ➔ Almost in the same conditions as PET
- ❖ Apparition of a low strain hardening for $\epsilon \geq 450\%$ (engineering curves)
- ❖ Development of a microstructural organization

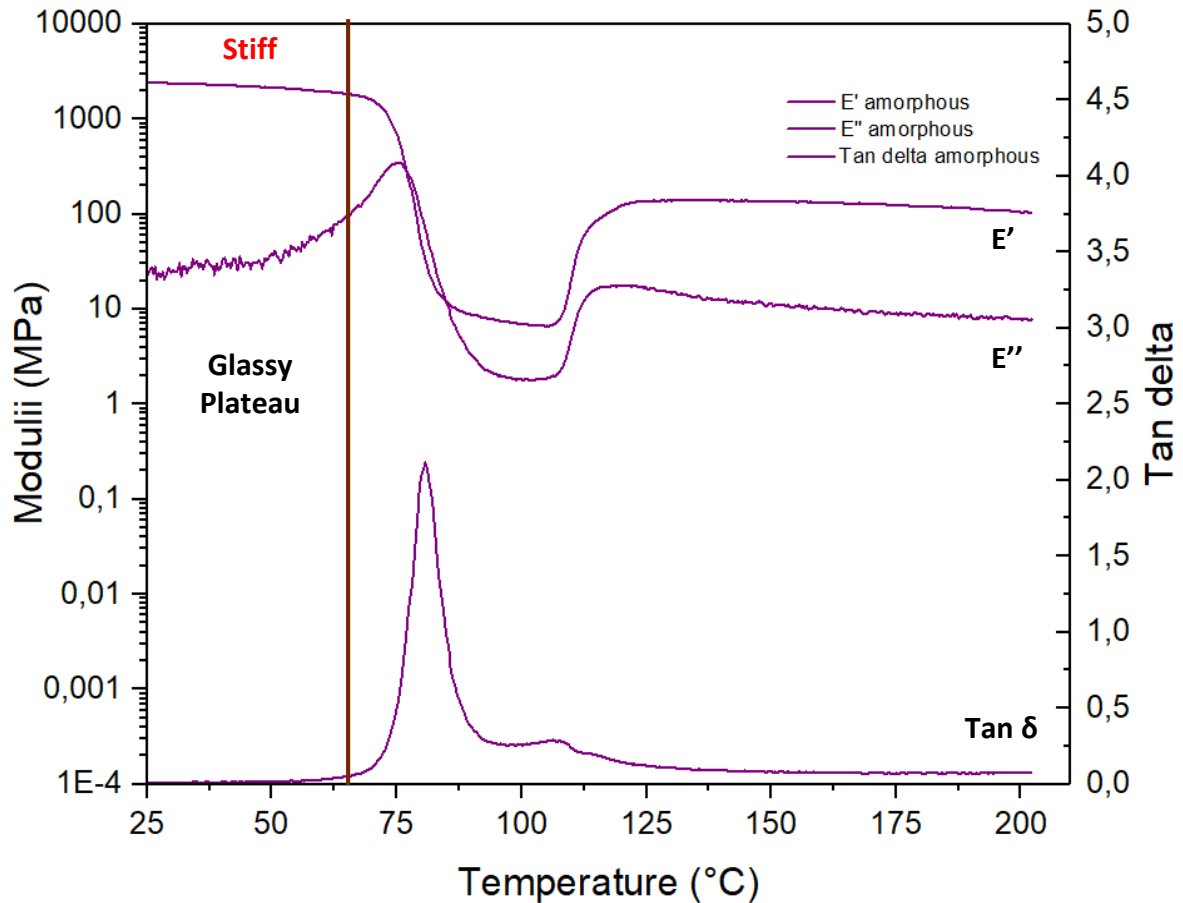


PET viscoelasticity

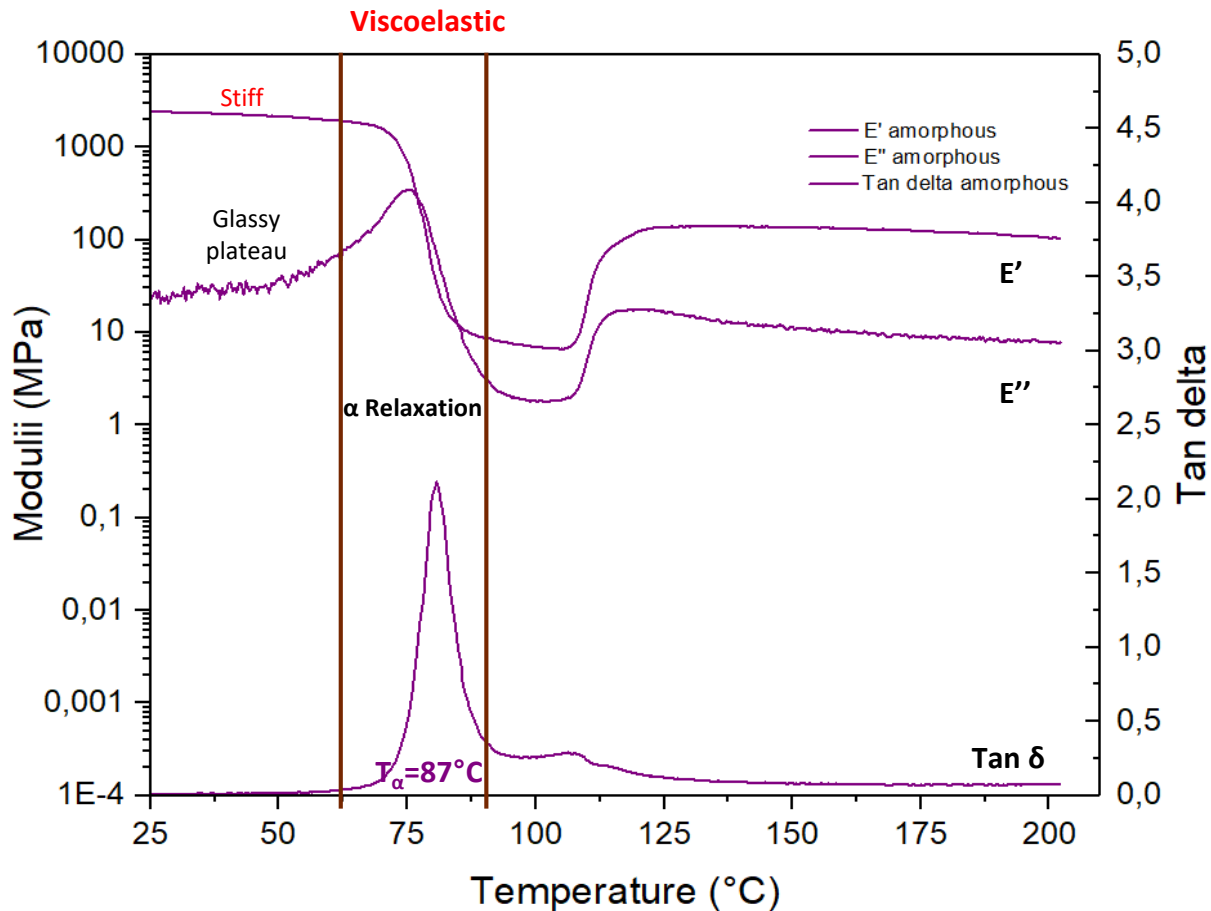
❖ Evolution of the stiffness according to the temperature (25-210°C), 1°C/min, 1Hz



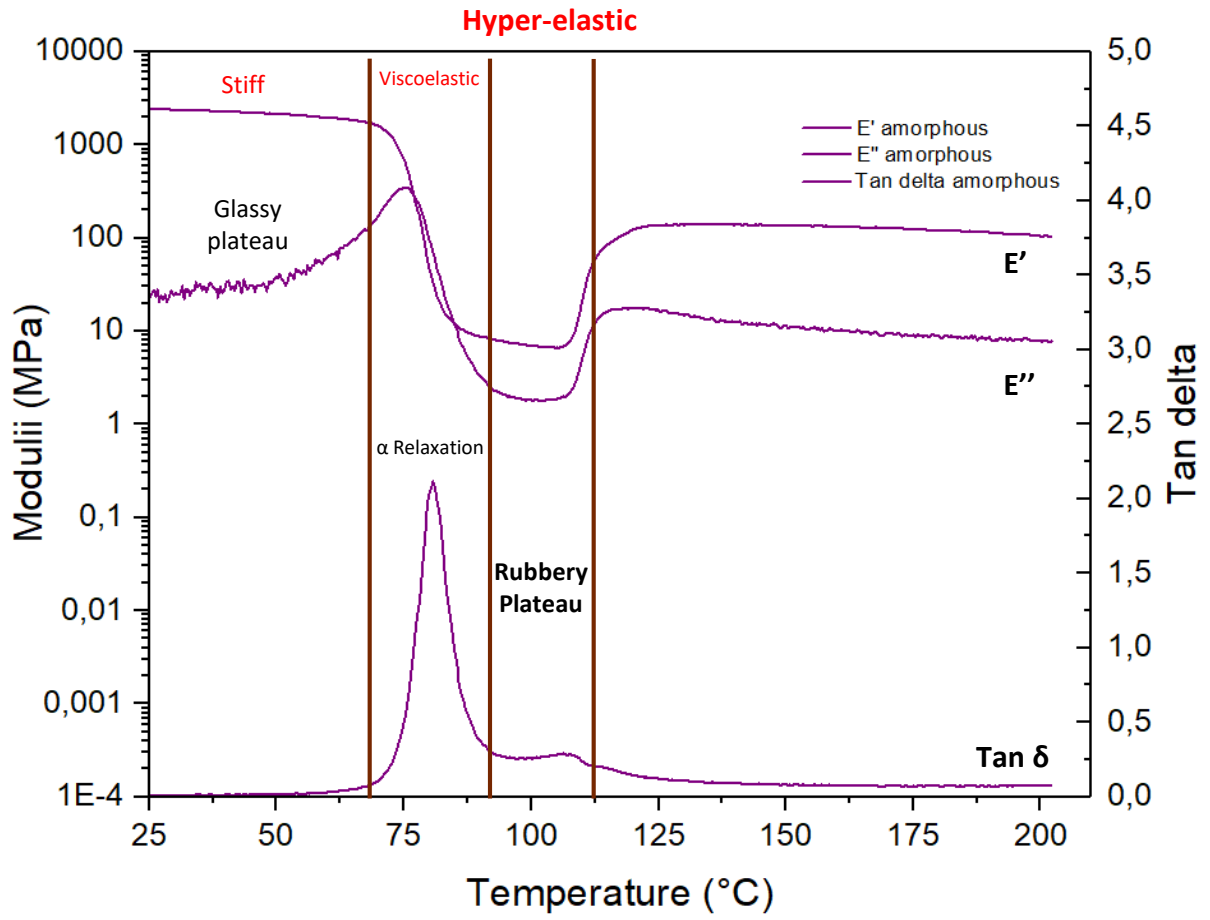
PET viscoelasticity



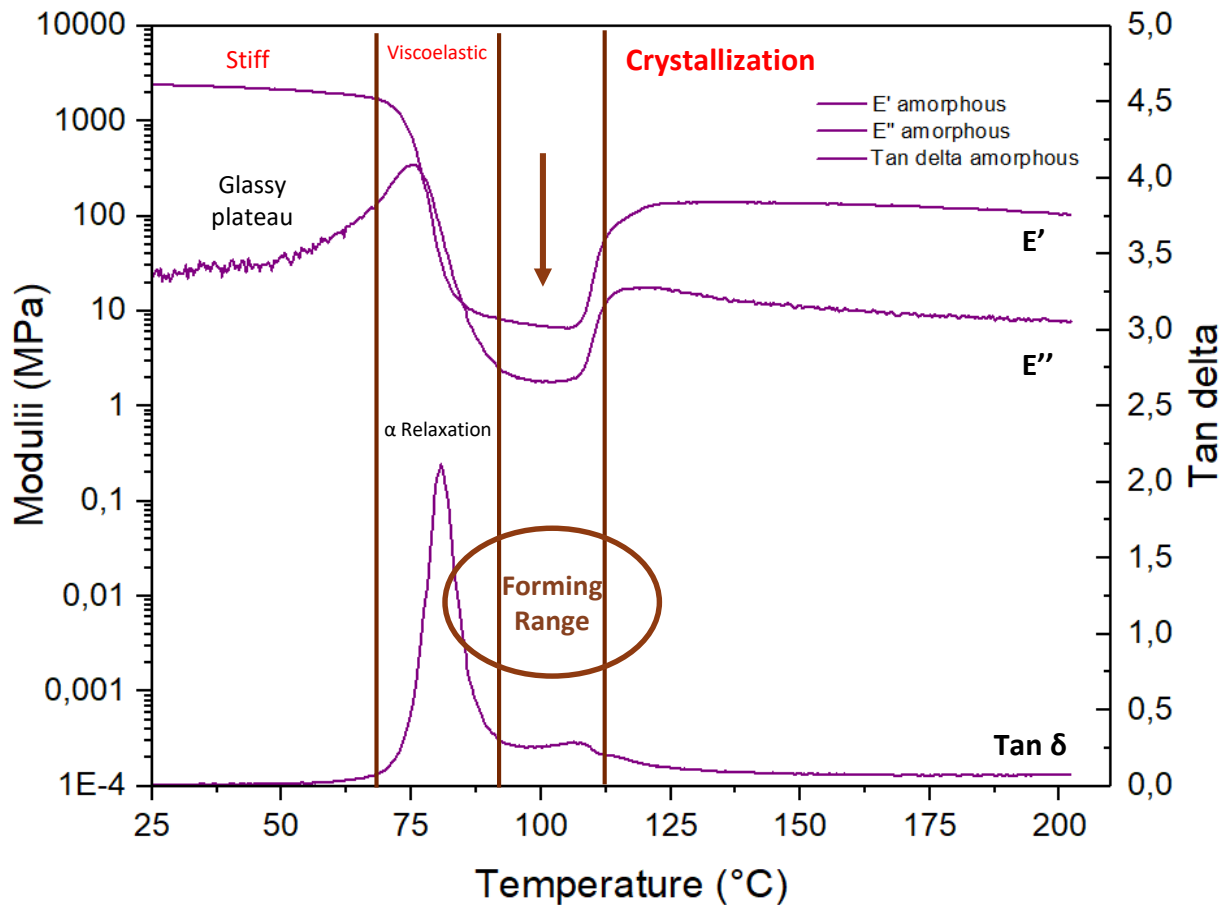
PET viscoelasticity



PET viscoelasticity

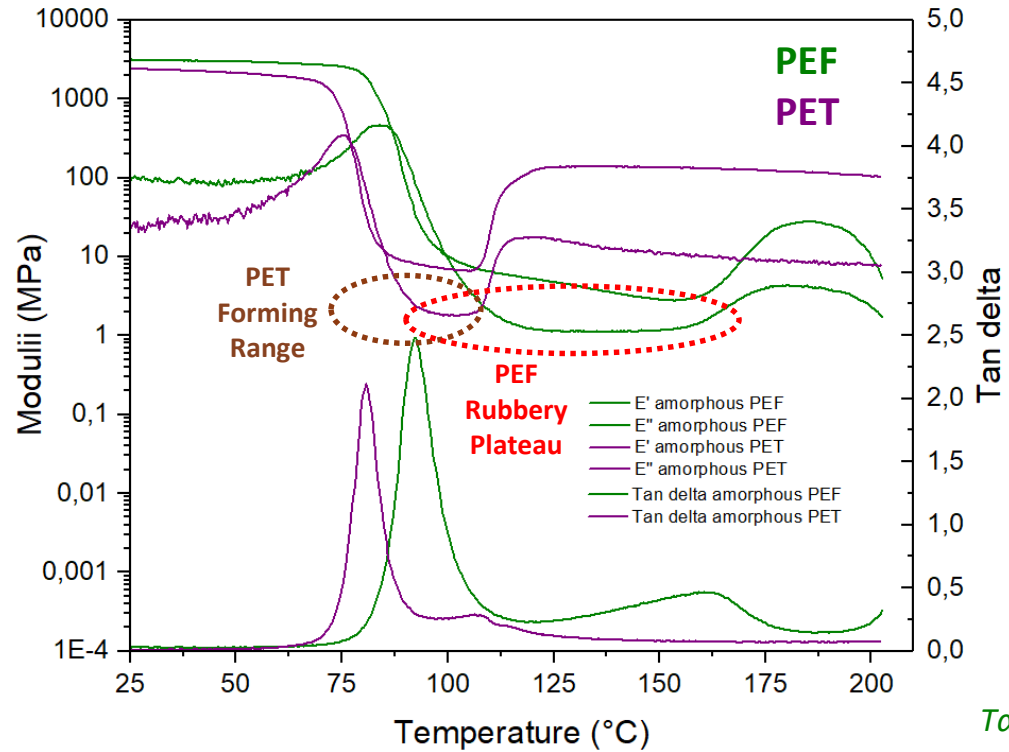


PET viscoelasticity



PEF and PET forming range

❖ Comparison of PET and PEF rubbery plateau



$T\alpha$ (1Hz) = 100°C
 $T\alpha$ (1Hz) = 87°C

→ PEF rubbery plateau appears later than PET one

→ PEF stretching range has to be different from the PET one



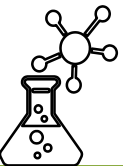
How to find PEF suitable stretching range to reach high deformations ?





- ❖ **Time/temperature principle**

- Building of master curves



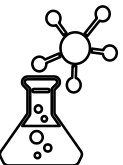


- ❖ Time/temperature principle

- Building of master curves

- ❖ **From the mastercurve to the uniaxial stretching**

- Mechanical behavior in large deformation domain





- ❖ **Time/temperature principle**

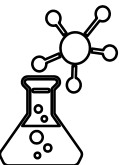
- Building of master curves

- ❖ **From the mastercurve to the uniaxial stretching**

- Mechanical behavior in large deformation domain

- ❖ **Microstructural development**

- Apparition of an organized microstructure



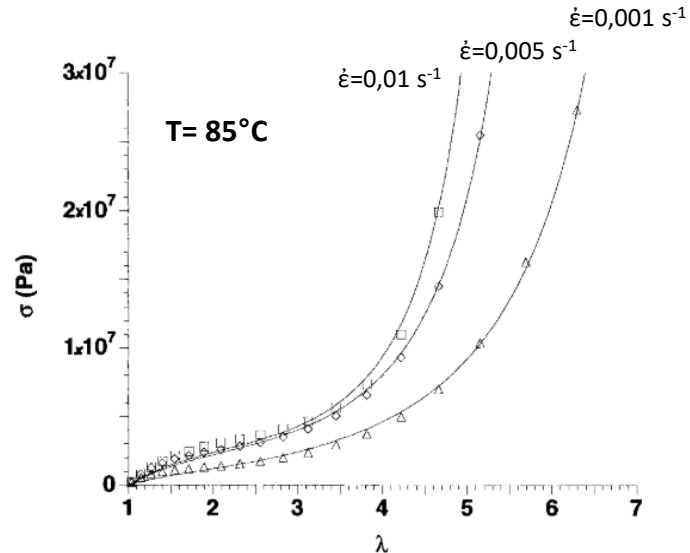
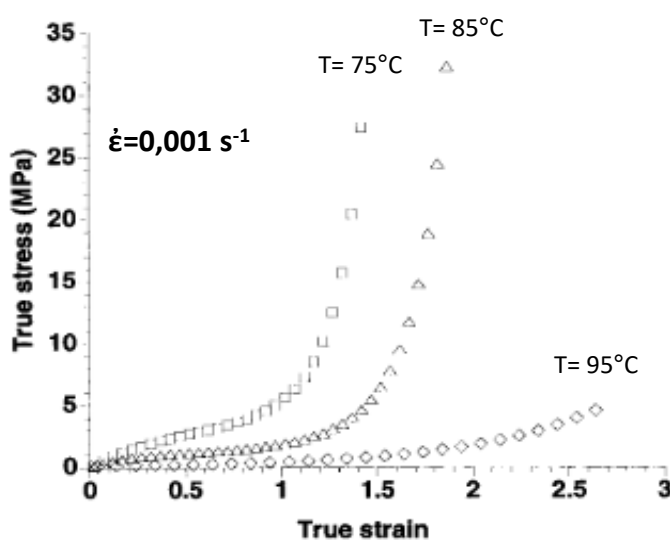


Time/temperature principle



1) Time/temperature dependence

- ❖ Existence of a dependence in time and temperature
- ❖ Possibility to describe it on the same graph ?
- Master curve at a reference temperature
- ❖ Description with an unique variable: **Equivalent strain rate at a reference temperature**



I) PEF frequency sweep

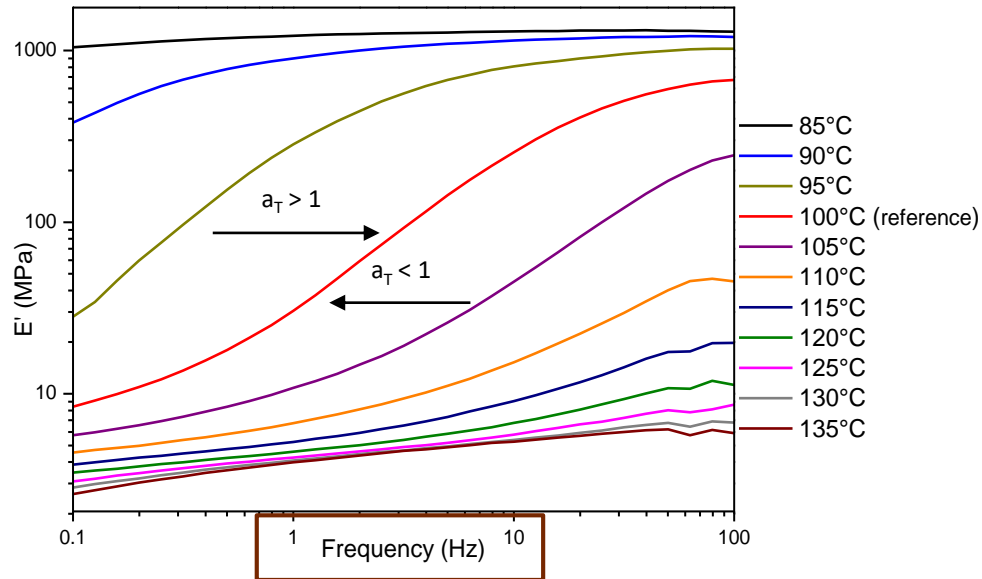
❖ Frequency sollicitation ($0,1 \text{ Hz} \leq f \leq 100 \text{ Hz}$) in the forming range

$90^\circ\text{C} \leq T \leq 140^\circ\text{C}$, isothermal step of 5°C

❖ Sweep of the scans on the reference temperature chosen close to the T_α ($f \rightarrow f * a_T$)

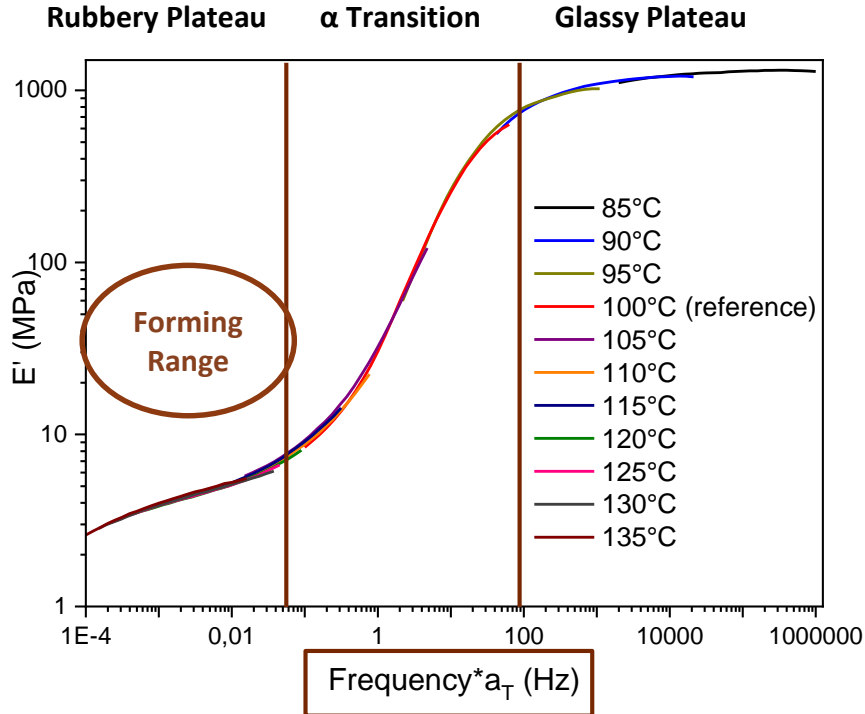
a_T : shift factor related to an unique temperature

$T_{\text{ref}} = 100^\circ\text{C}$ (PEF)
 $T_{\text{ref}} = 90^\circ\text{C}$ (PET)



I) PEF master curve with $T_{ref} = 100^{\circ}\text{C}$

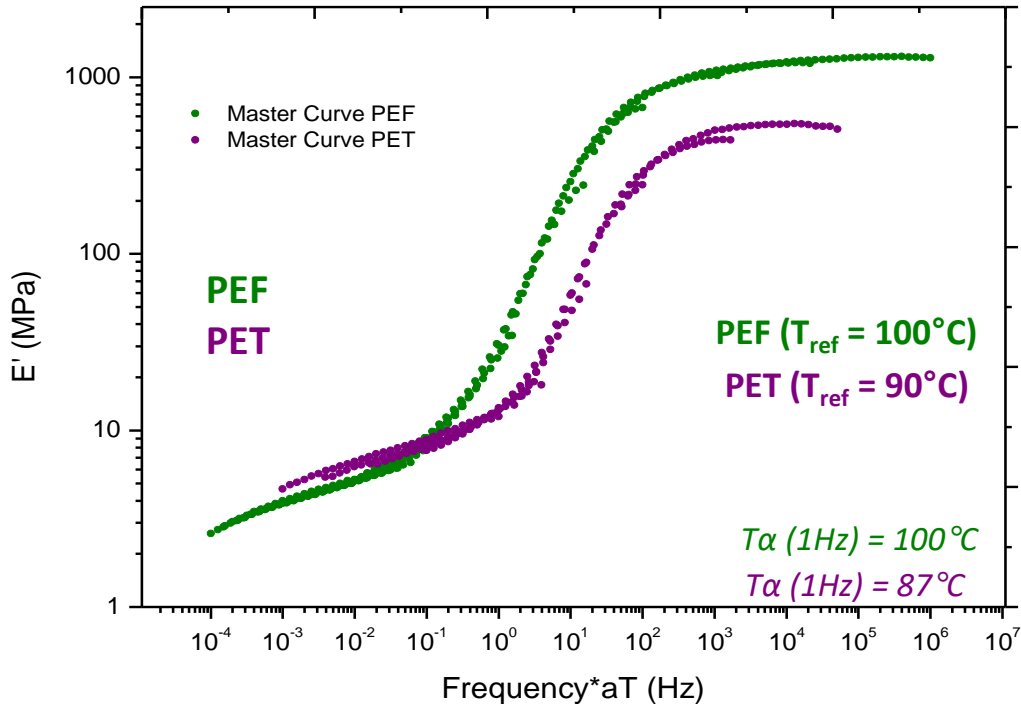
- ❖ Description of the mechanical behaviour on a large frequency range
- ❖ Description of the material state depending on the frequency and the temperature



→ PEF mechanical behaviour can be modeled by a master curve

I) Master curves

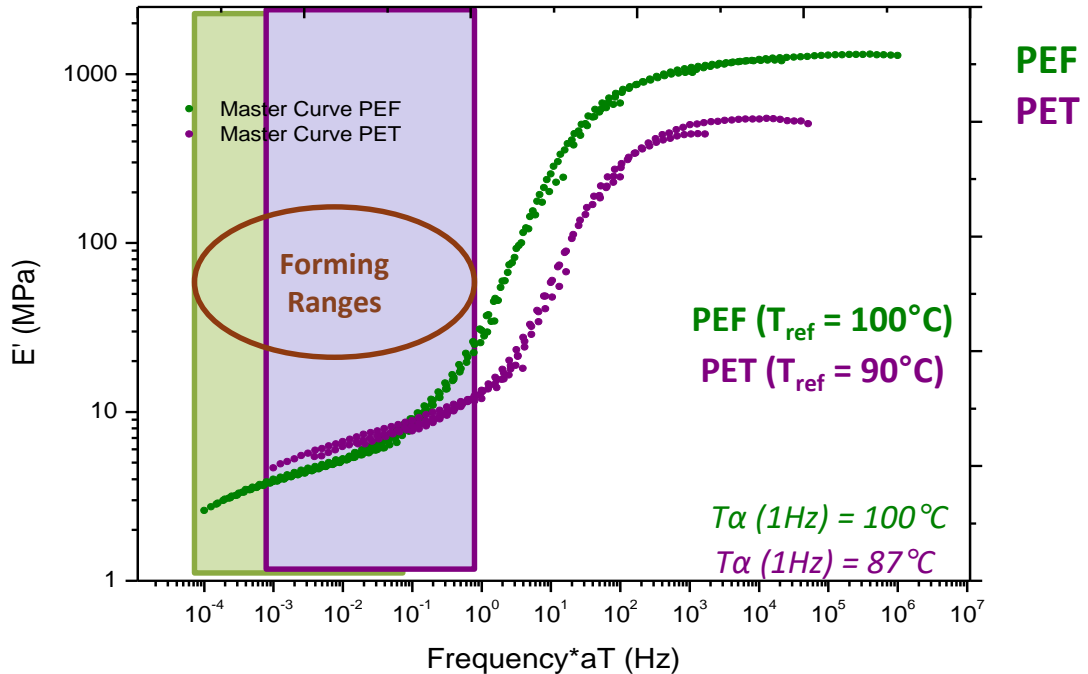
- ❖ Realization of two master curves at two different reference temperatures chosen close to the $T\alpha$



→ PEF and PET master curves are close

I) Forming range

- ❖ Realization of two master curves at two different reference temperatures chosen close to the $T\alpha$



→ Superposition of PEF and PET forming ranges



PEF and PET uniaxial stretching



II) Choice of the stretching conditions

❖ Hypothesis: $f * a_T \approx \dot{\epsilon} * a_T$ ($\dot{\epsilon}$: strain rate s^{-1}) = equivalent strain rate

❖ Calculation of $\dot{\epsilon}$

→ Example: $\dot{\epsilon} * a_T = 0,01 s^{-1} \rightarrow \dot{\epsilon} = \frac{0,01}{a_T} s^{-1}$ (a_T : shift factor dependent on the temperature)

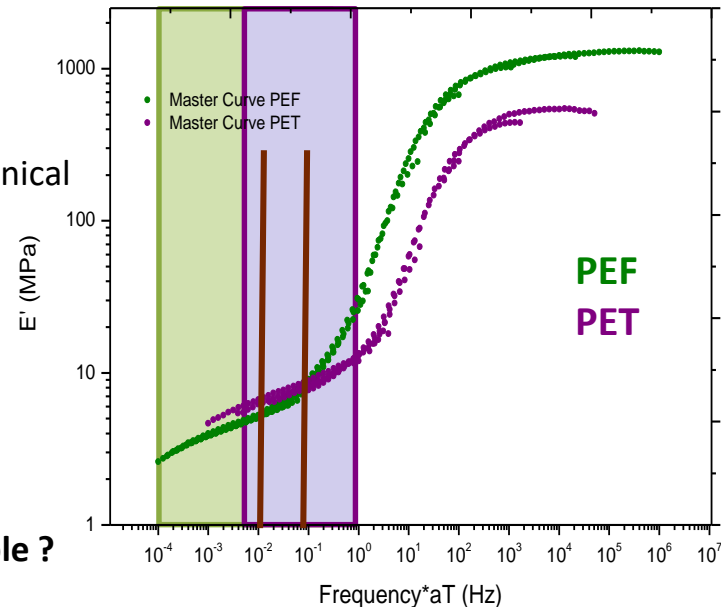
❖ Exploration of the master curve: $\dot{\epsilon} * a_T = 0,01$ and $0,1 s^{-1}$

❖ For PEF and PET

→ Master curve = same reference state

→ Same position on the curve = same mechanical behaviour

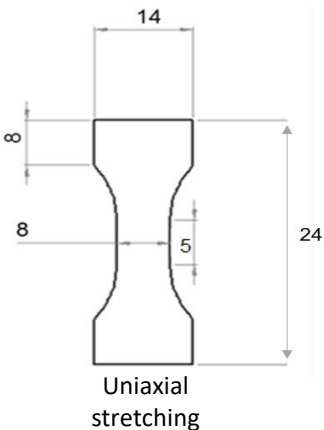
❖ Validity of the time/temperature principle ?



II) Etifi presentation

Step*Filter size	Subset
3*13	31

- ❖ Samples withdrawn from extruded sheets of 700 μ m of thickness
- ❖ Hot uni-axial stretching until rupture (exponential velocity)
- ❖ Optical measurement (1 camera): DIC
- ❖ Thermal measurement (pyrometer)
- ❖ 5 minutes of preheating/ air quenched



Pyrometer

Window transparent to IR
ZnSe (T=70%)

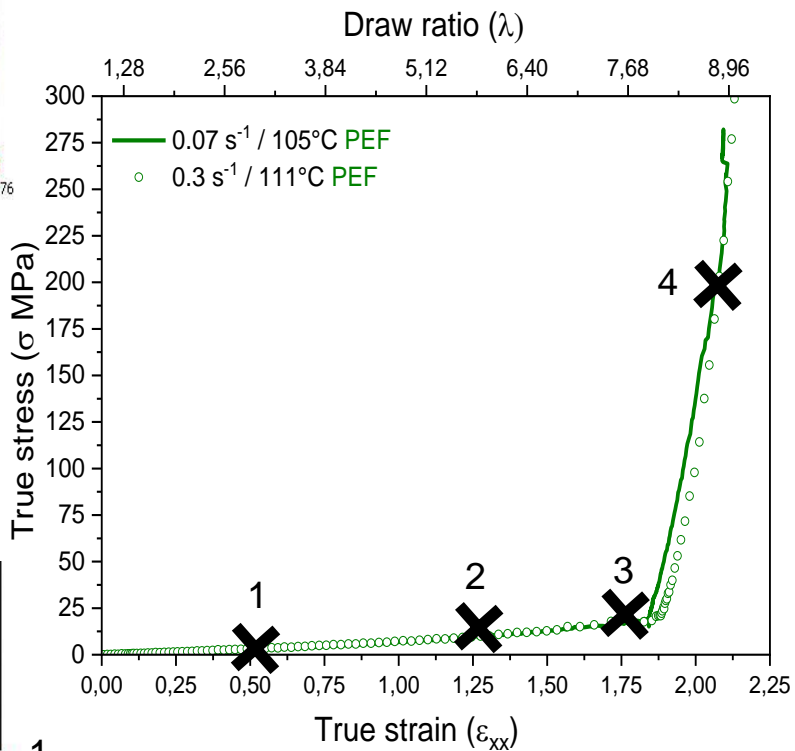
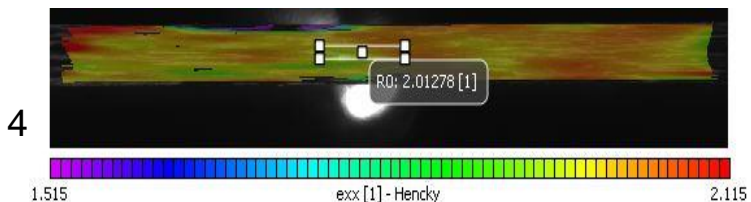
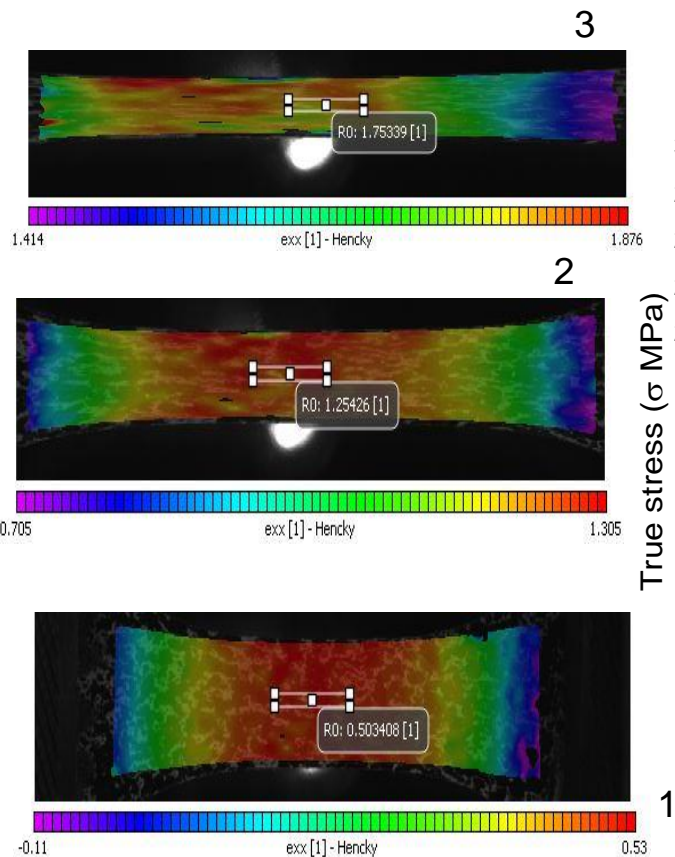
Window transparent to visible radiation
Pyrex

Camera



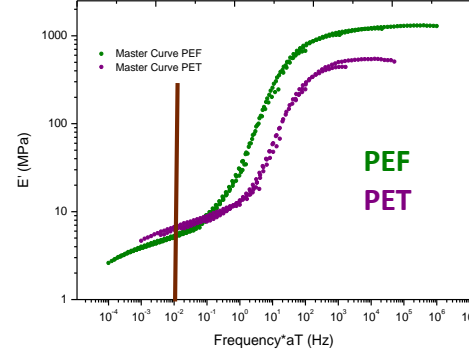
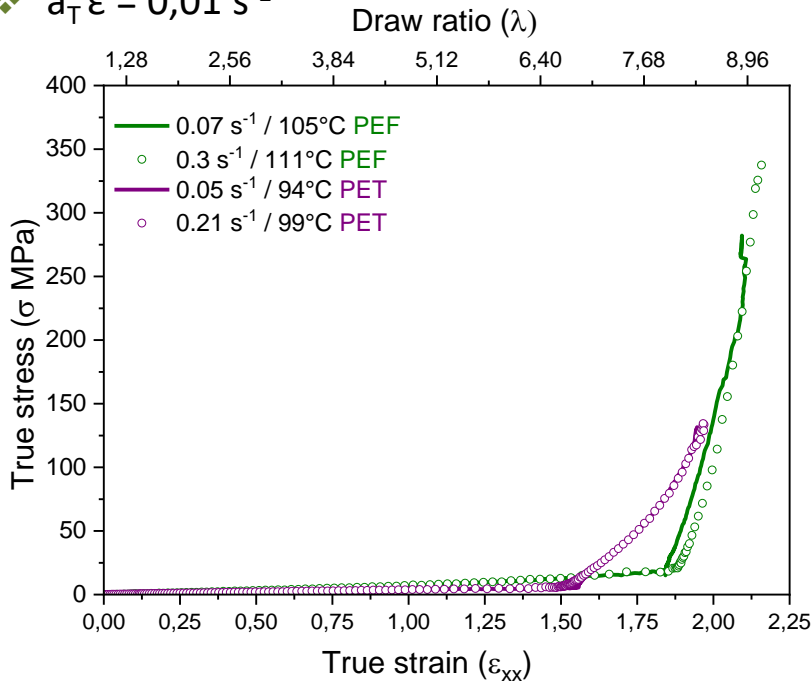
II) PEF uniaxial stretching

$$\diamond a_T \dot{\epsilon} = 0,01 \text{ s}^{-1}$$



II) Uniaxial deformation

$$a_T \dot{\epsilon} = 0,01 \text{ s}^{-1}$$

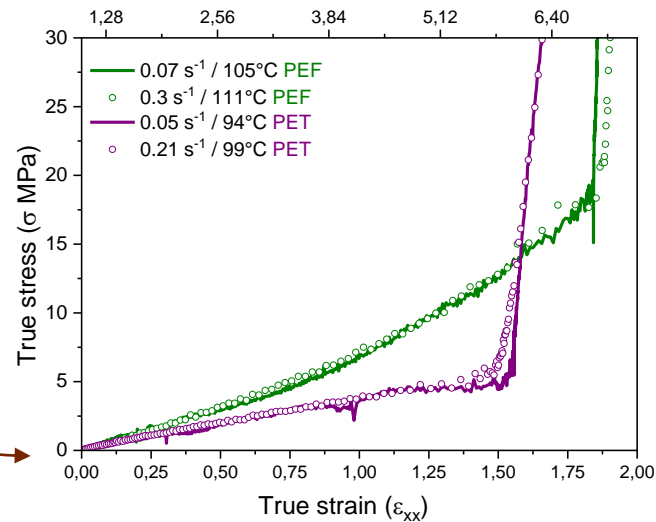
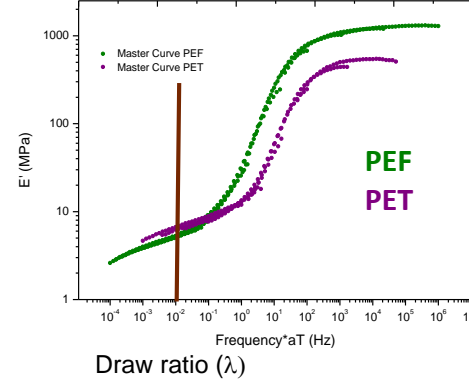
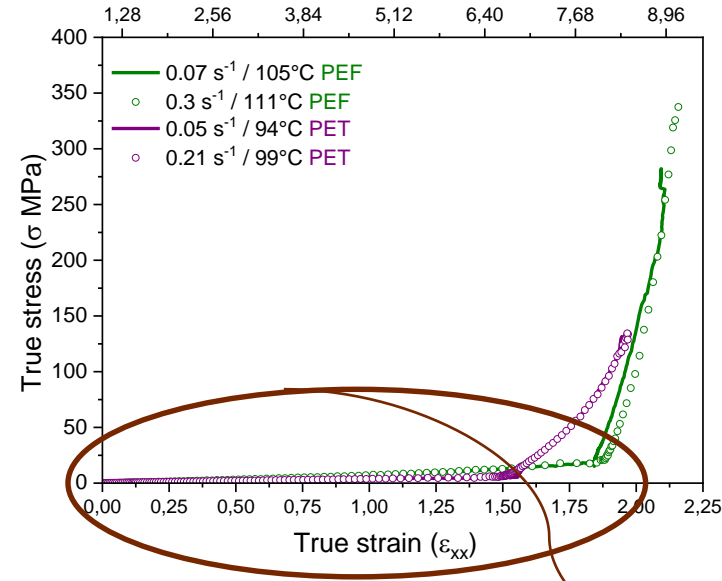


- Validity of the time/temperature principle for both
- Strain hardening is postponed for PEF
- Slope of the strain hardening sharper for PEF

II) Uniaxial deformation

$a_T \dot{\epsilon} = 0,01 \text{ s}^{-1}$

Draw ratio (λ)

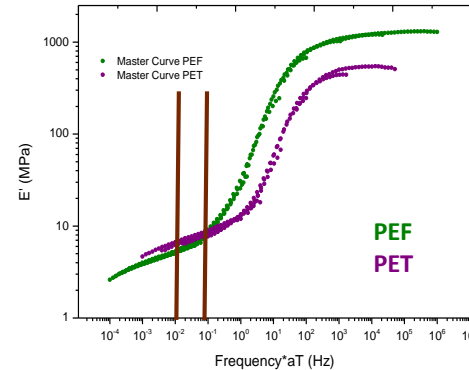
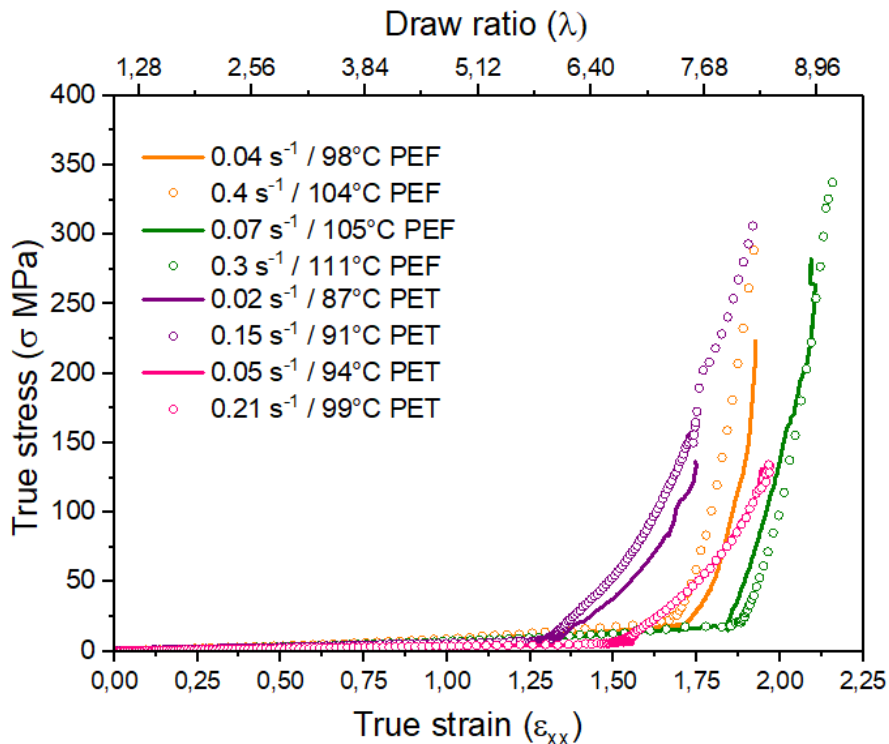


→ Same order of magnitude

→ Materials with a low stiffness and a high strain hardening

II) Uniaxial deformation

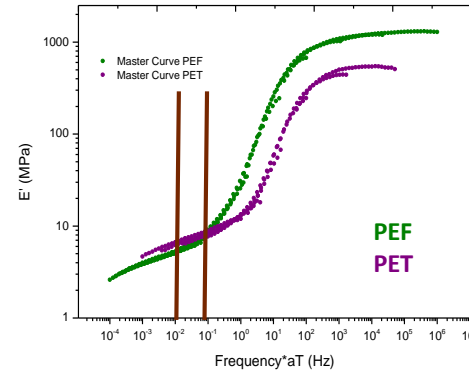
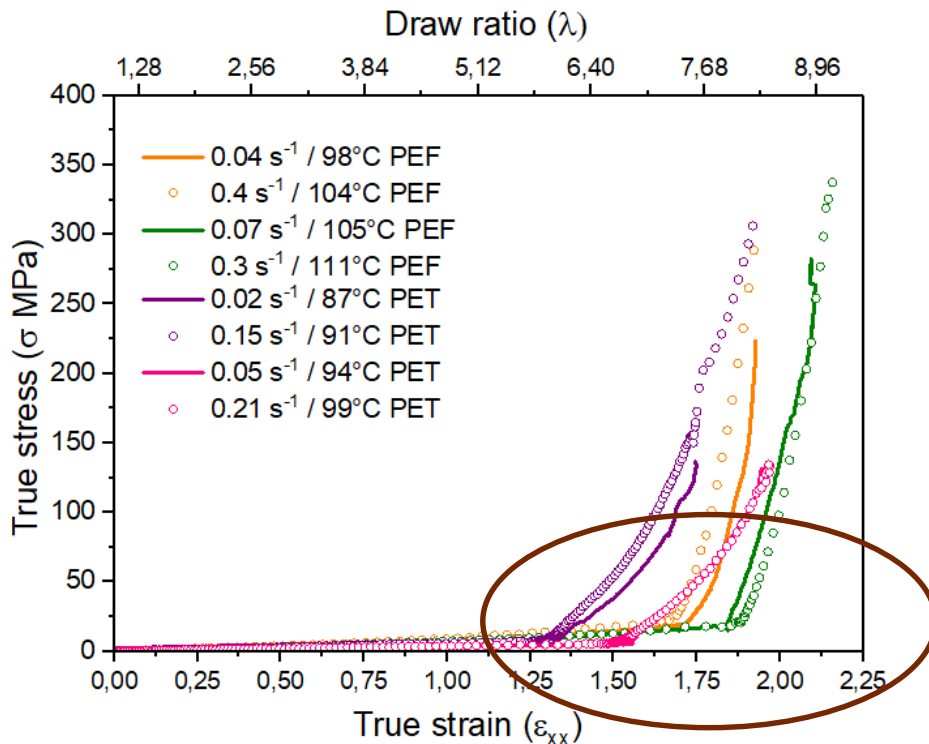
❖ $a_T \dot{\epsilon} = 0,1 \text{ s}^{-1}$ and $0,01 \text{ s}^{-1}$



→ Validity of time/temperature principle for others equivalent strain rate

II) Uniaxial deformation

❖ $a_T \dot{\epsilon} = 0,1 \text{ s}^{-1}$ and $0,01 \text{ s}^{-1}$



Strain hardening appears later when $\dot{\epsilon} * a_T$ decreases

→ Validity of time/temperature principle for others equivalent strain rate

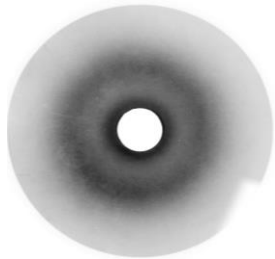


Microstructural development



III) Apparition of an organized microstructure

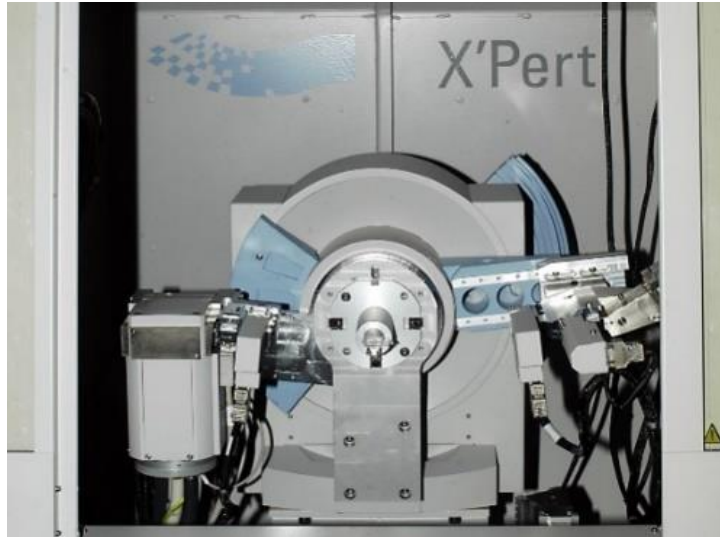
- ❖ Characterization of the orientation by a Debye-Scherrer in plane chamber analysis



Amorphous
PEF

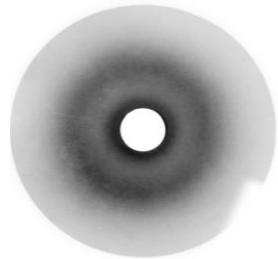


Amorphous
PET



III) Apparition of an organized microstructure

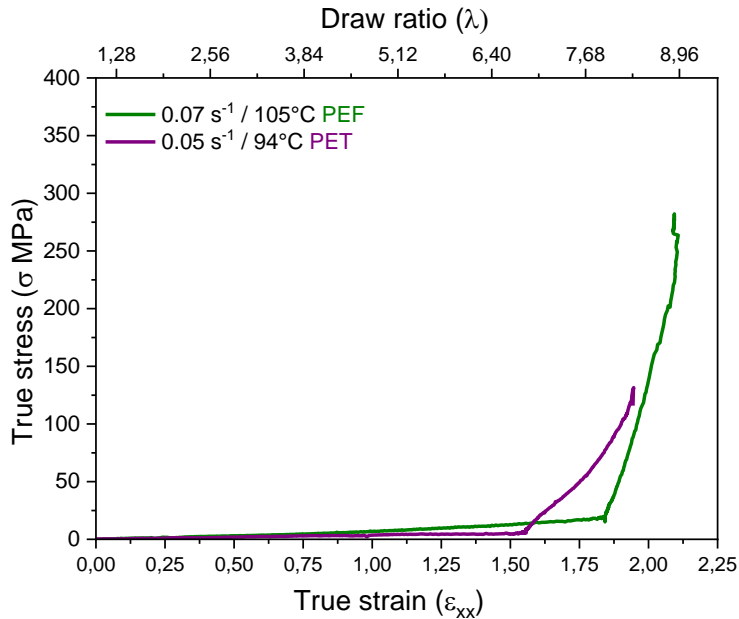
- ❖ Characterization of the orientation by a Debye-Scherrer in plane chamber analysis



Amorphous
PEF

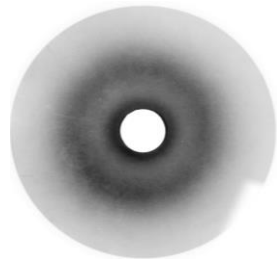


Amorphous
PET

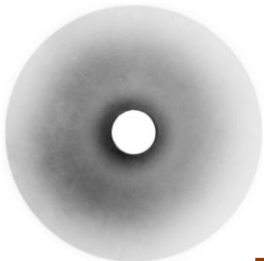


III) Apparition of an organized microstructure

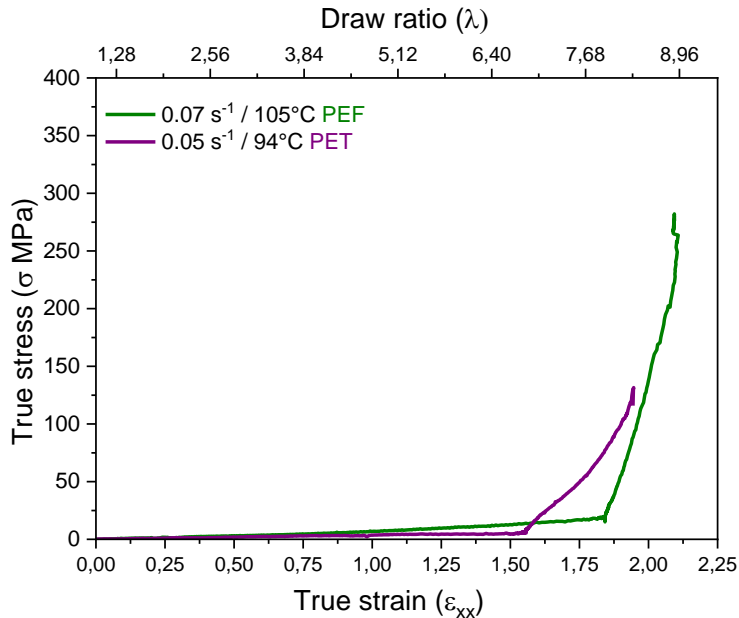
- ❖ Characterization of the orientation by a Debye-Scherrer in plane chamber analysis
- ❖ After the stretching: semi-crystalline material



Amorphous
PEF



Amorphous
PET



Semi-crystalline
PEF

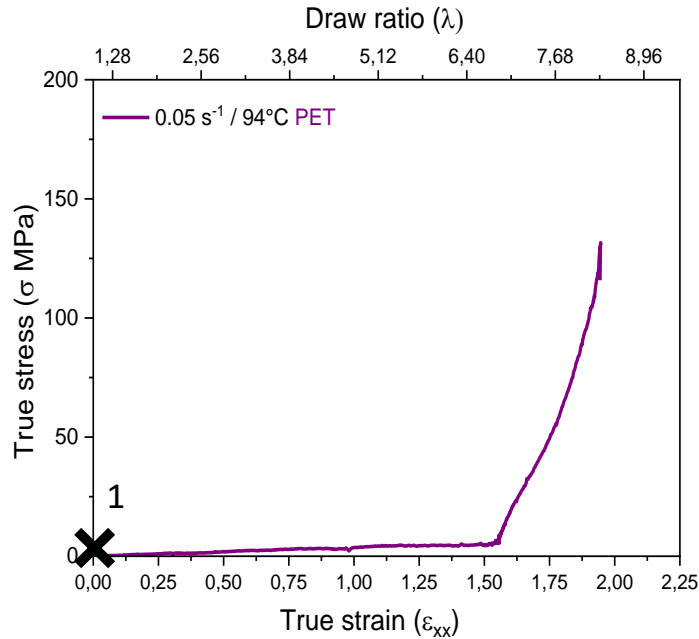


Semi-crystalline
PET

→ Evolution of the microstructure during the stretching?

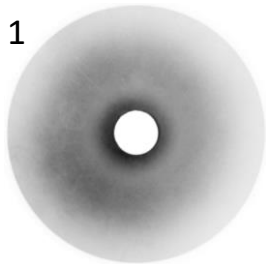
III) Apparition of an organized microstructure

❖ Interrupted tests during the loading

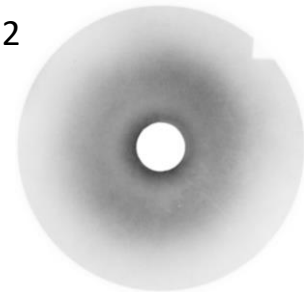


III) Apparition of an organized microstructure

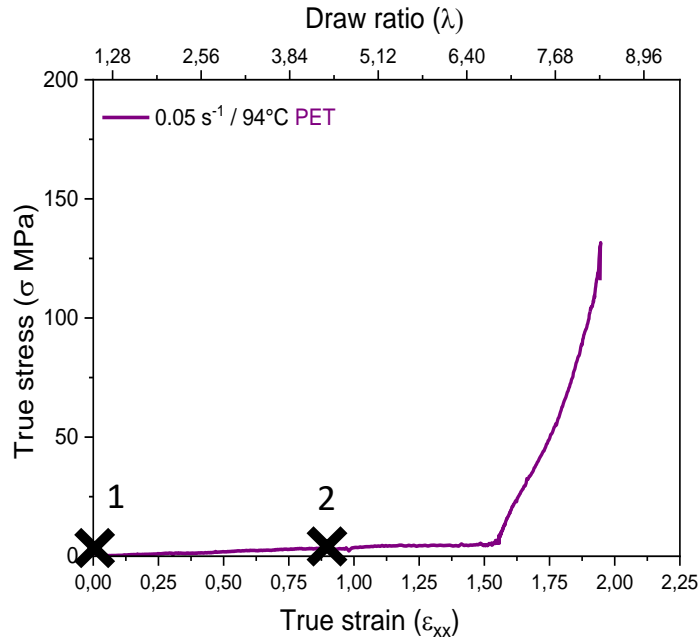
❖ Interrupted tests during the loading



Amorphous
PET

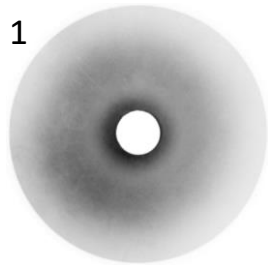


$$\epsilon_{xx} = 0,9$$

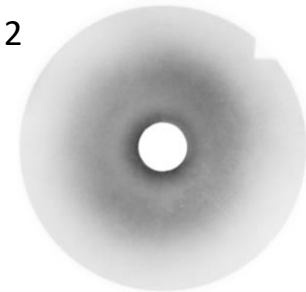


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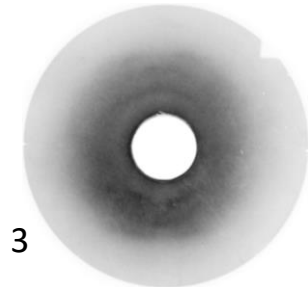
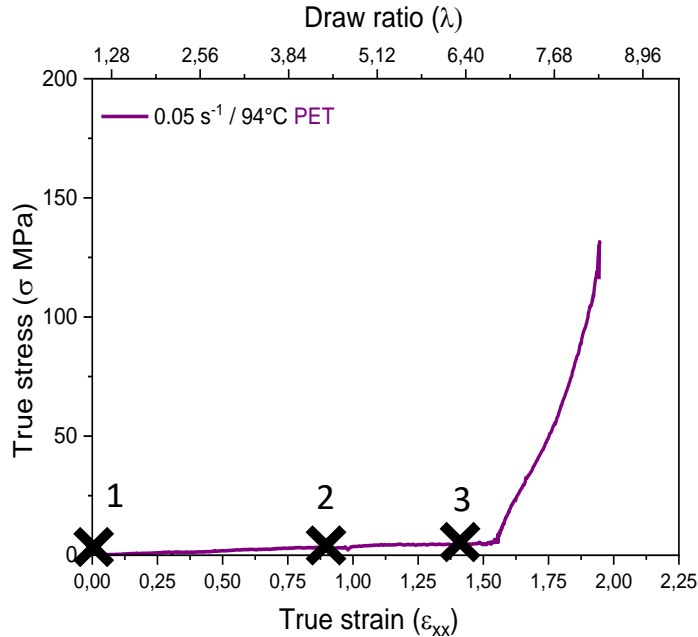
❖ Interrupted tests during the loading



Amorphous
PET



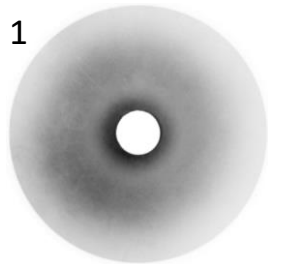
$\epsilon_{xx} = 0,9$



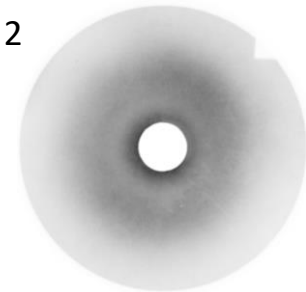
$\epsilon_{xx} = 1,45$

III) Apparition of an organized microstructure

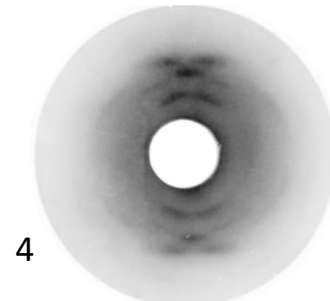
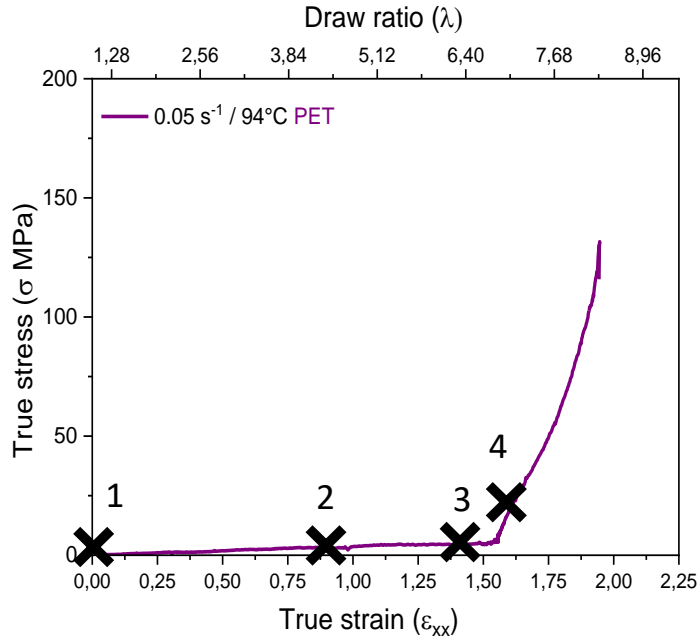
❖ Interrupted tests during the loading



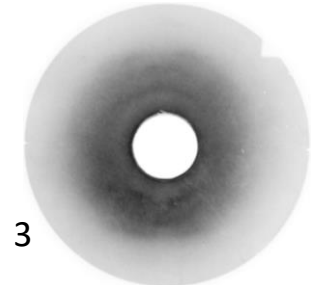
Amorphous
PET



$\epsilon_{xx} = 0,9$



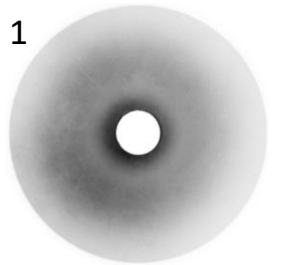
$\epsilon_{xx} = 1,6$



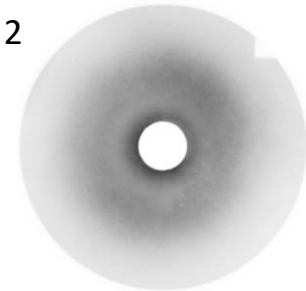
$\epsilon_{xx} = 1,45$

III) Apparition of an organized microstructure

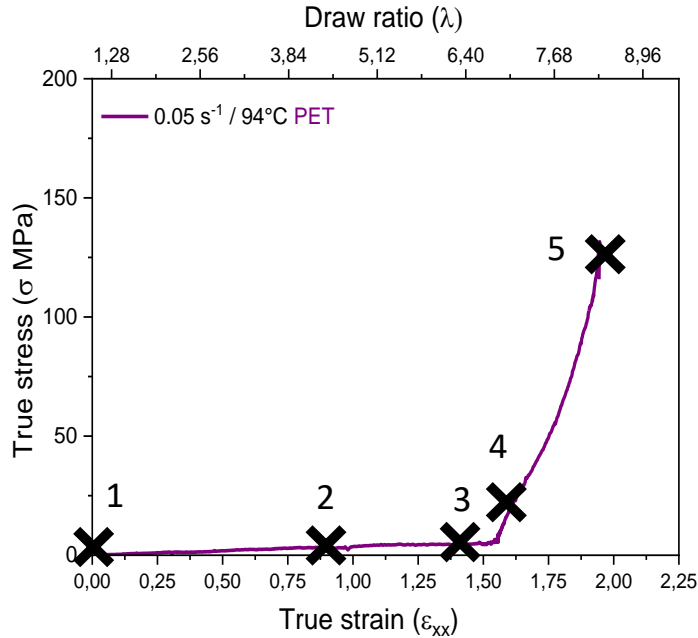
❖ Interrupted tests during the loading



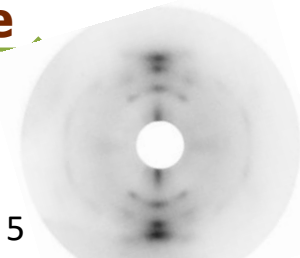
Amorphous
PET



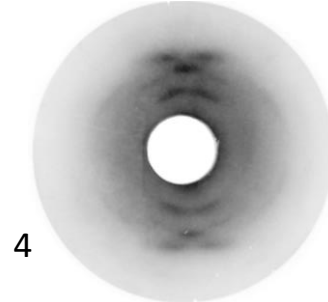
$\epsilon_{xx} = 0,9$



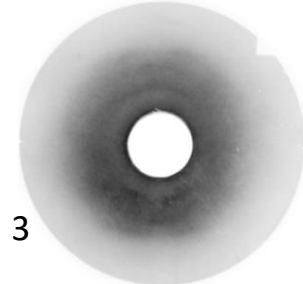
→ Texturation after the stretching in PET



Semi-crystalline
PET



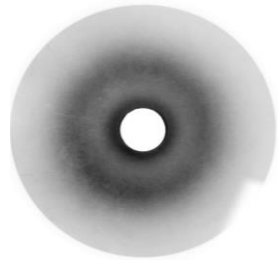
$\epsilon_{xx} = 1,6$



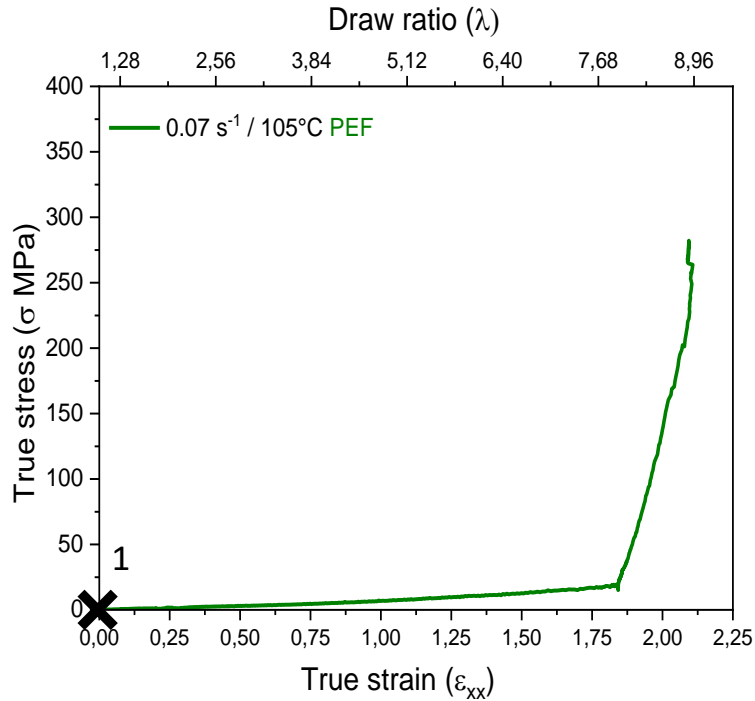
$\epsilon_{xx} = 1,45$

III) Apparition of an organized microstructure

- ❖ Interrupted tests during the loading

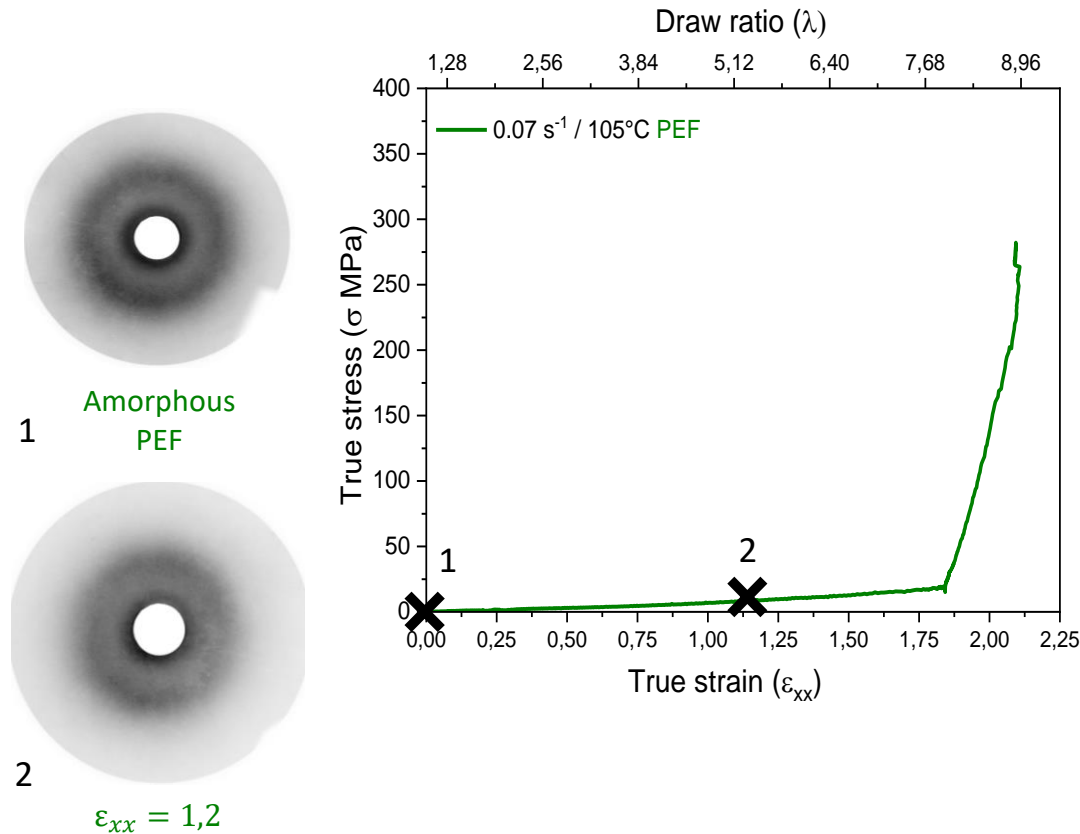


1
Amorphous
PEF



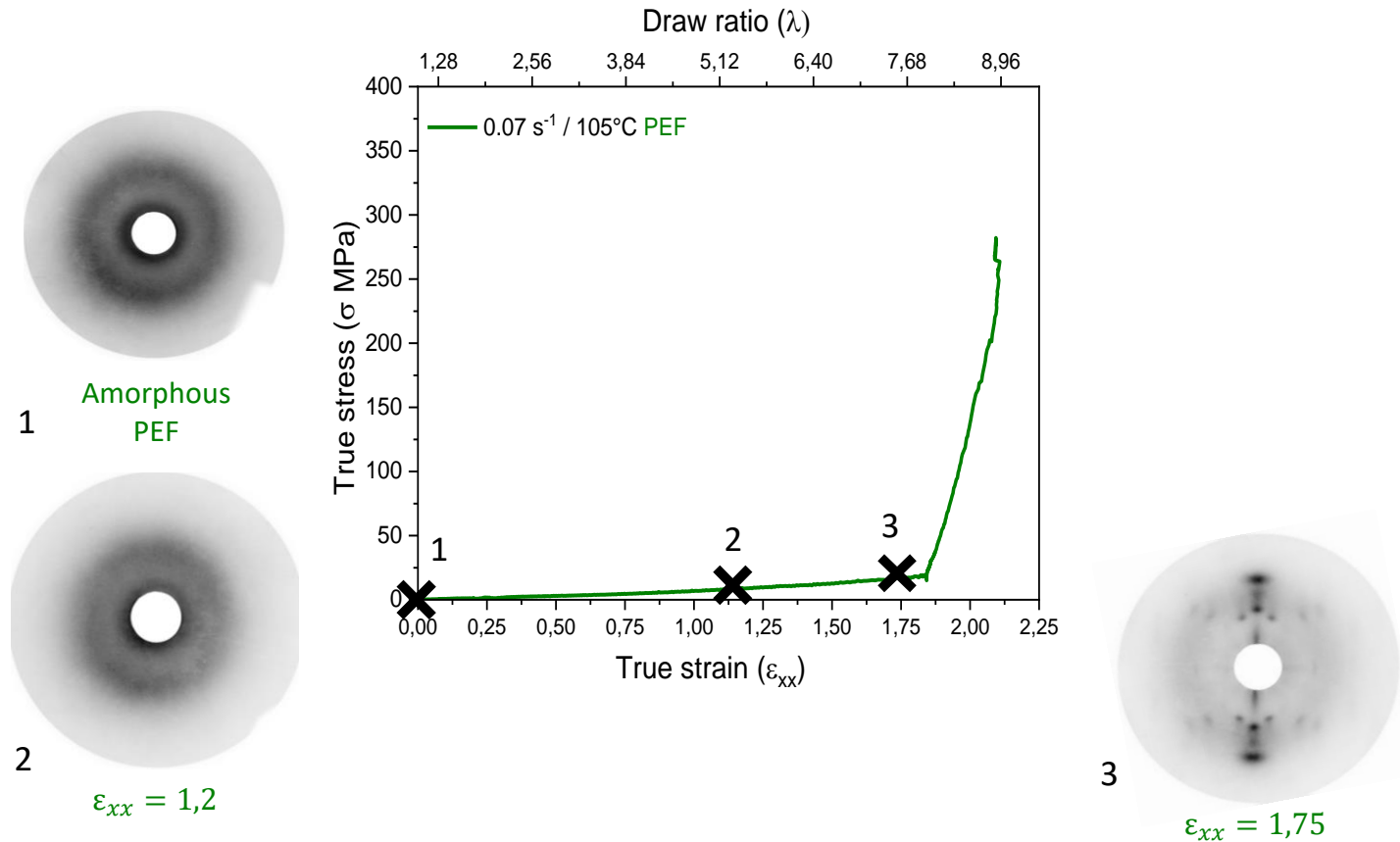
III) Apparition of an organized microstructure

- ❖ Interrupted tests during the loading



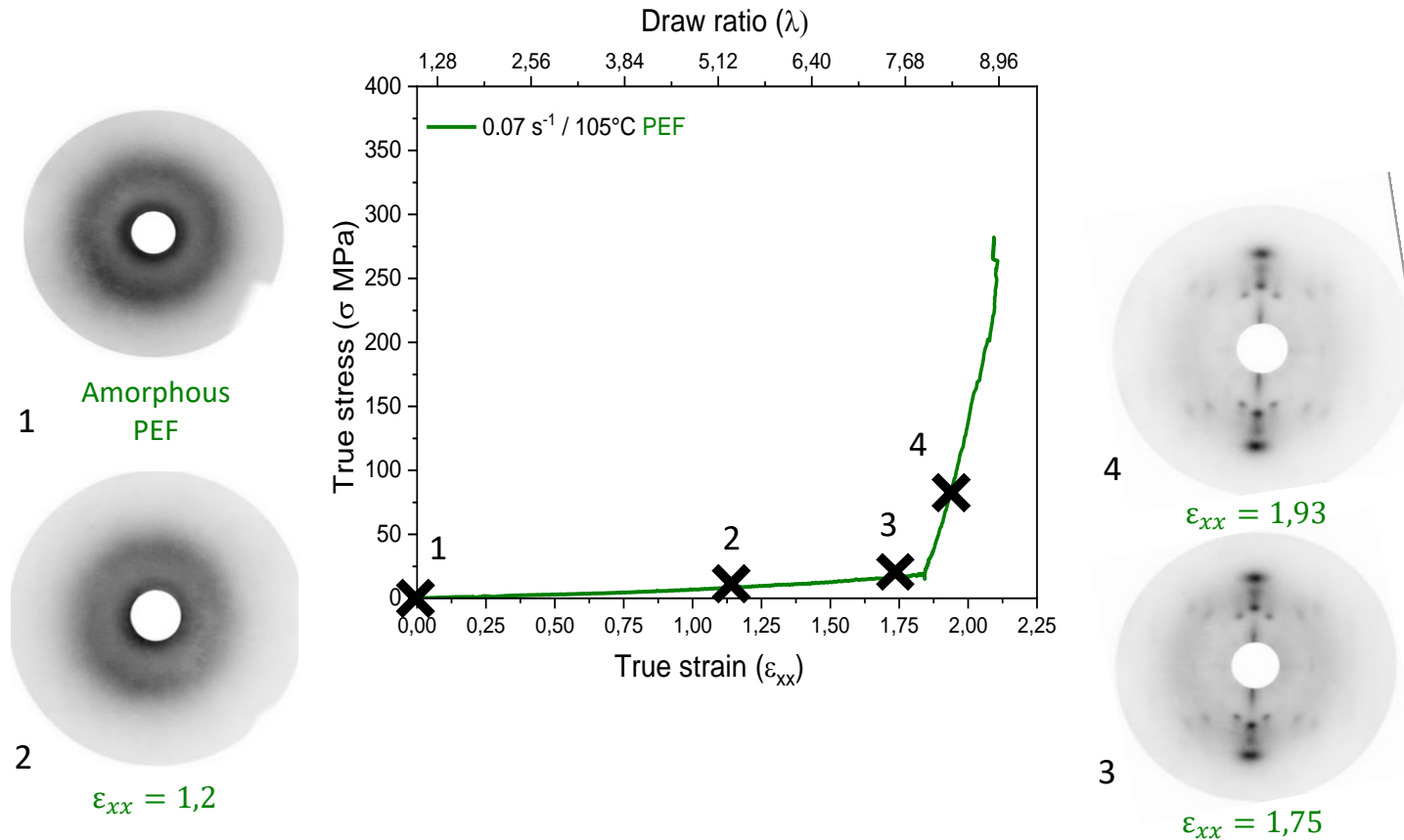
III) Apparition of an organized microstructure

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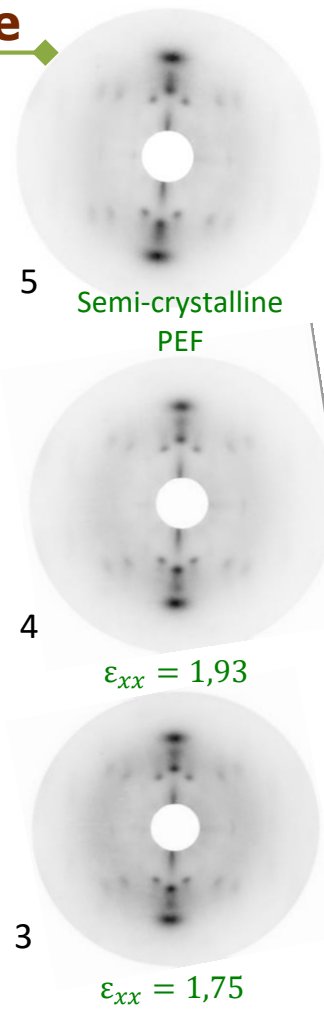
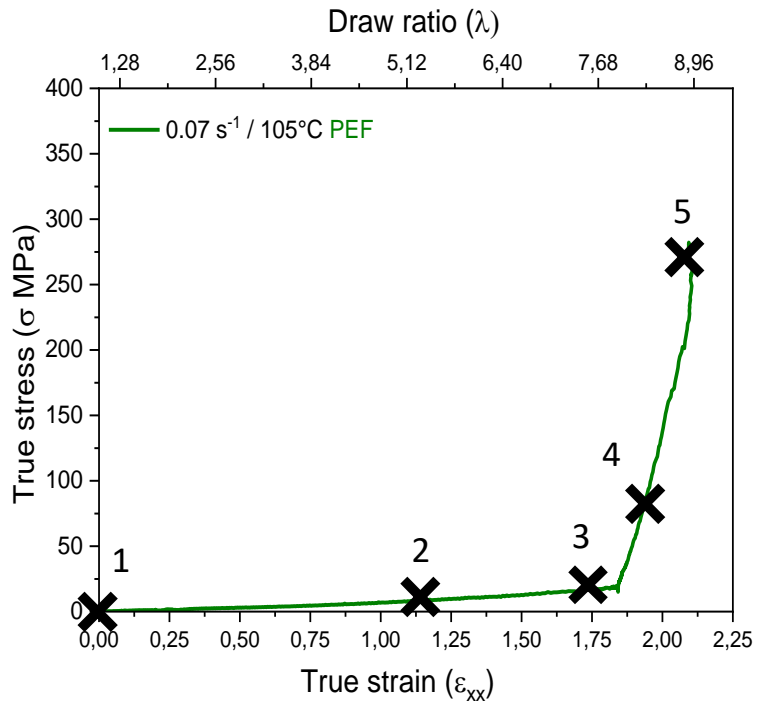
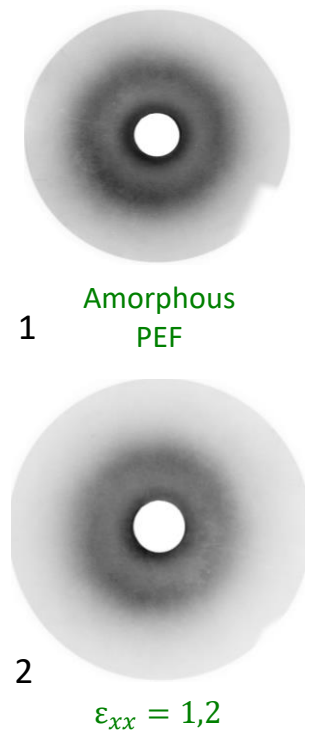
III) Apparition of an organized microstructure

❖ Interrupted tests during the loading



III) Apparition of an organized microstructure

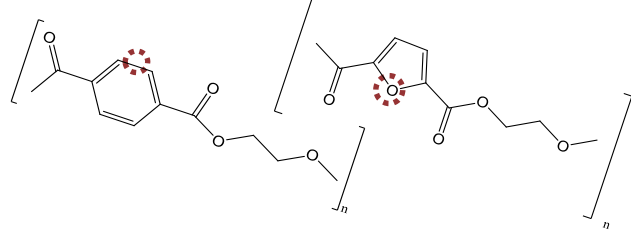
❖ Interrupted tests during the loading



➔ Texturation before the strain hardening in PEF

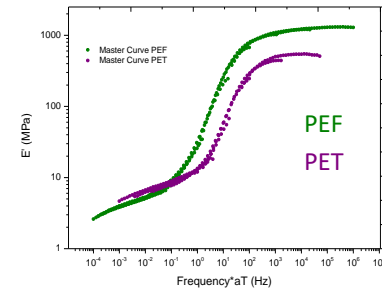
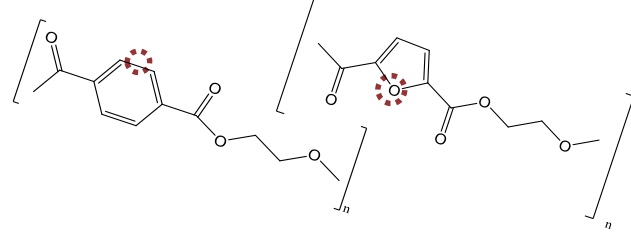
Conclusions

- ❖ Two molecules: PEF and PET
- ❖ PET stretching is known for several years
- ❖ PEF is relative new and is most of the time stretched as PET = low strain hardening

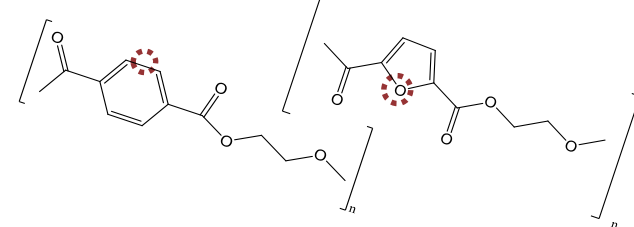


Conclusions

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- ❖ PET stretching is known for several years
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- ❖ Building of two master curves which are the starting point to find the suitable stretching conditions
- ❖ Validation of the time/temperature principle
- ❖ PEF can reach higher draw ratio than PET



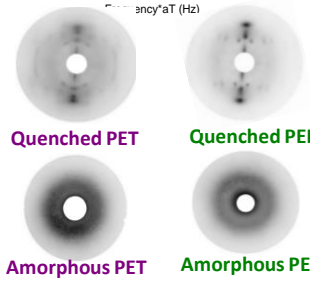
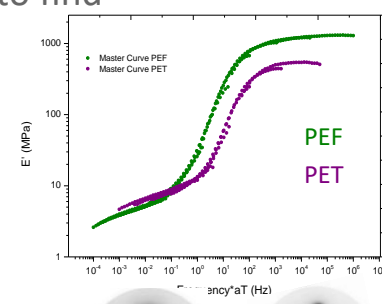
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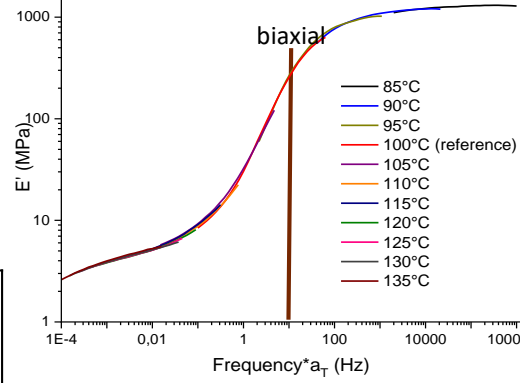
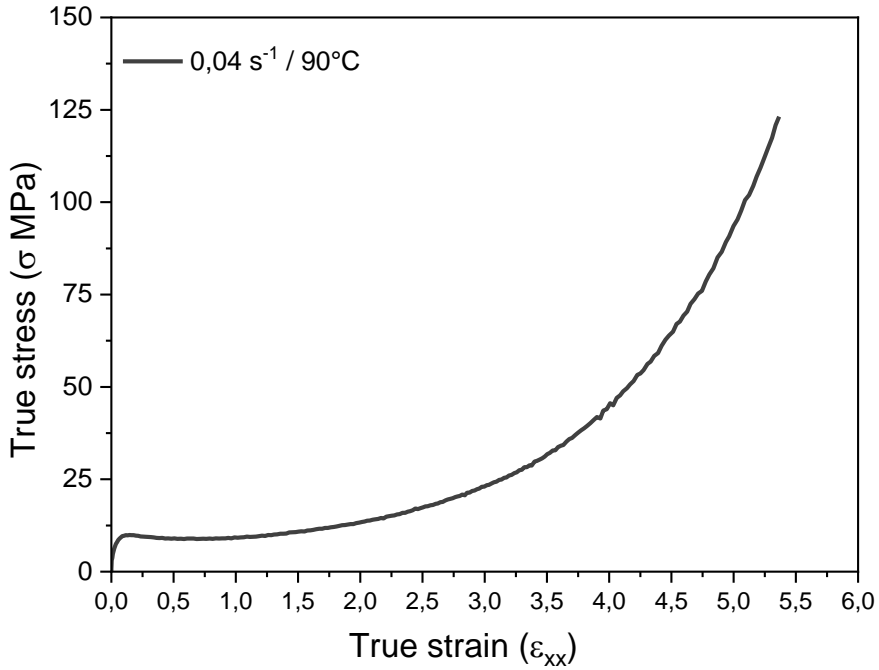
- ❖ Building of two master curves which are the starting point to find the suitable stretching conditions
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- ❖ Creation of an organized microstructure in PEF and PET
- ❖ Microstructural organization begins before the strain hardening for PEF and after for PET

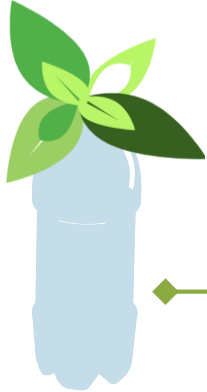


PEF biaxial stretching

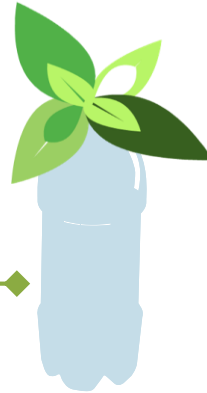
❖ $a_T \dot{\epsilon} = 10 \text{ s}^{-1}$



➔ PEF is able to strain harden in biaxial stretching



! Thanks for your attention !



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