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EFFECT OF STRESS RELAXATION ON MECHANICALLY INDUCED CRYSTALLIZATION IN NATURAL RUBBER

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Context & Objectives

The usual ways of measuring crystallization in a material are as follows:

- Nuclear magnetic resonance, differential scanning calorimetry, density measures
 - Wide Angle X-ray Diffraction
- no in-situ follow-up
choice of exposure time, synchrotron proposals, complex post-treatment ...



$$\Delta\theta, \underline{\sigma}, \underline{\epsilon}, \dots \rightarrow \underline{\chi_c}$$

The original approach proposed in this thesis is to be able to measure crystallinity levels using **infrared thermography** and then use a conversion model to obtain a map of crystallinity, and particularly for complex cases: **heterogeneous fields, crack bifurcation**, etc. Before setting up such a model, it is necessary to **better understand certain microstructural phenomena** involved in crystallization.

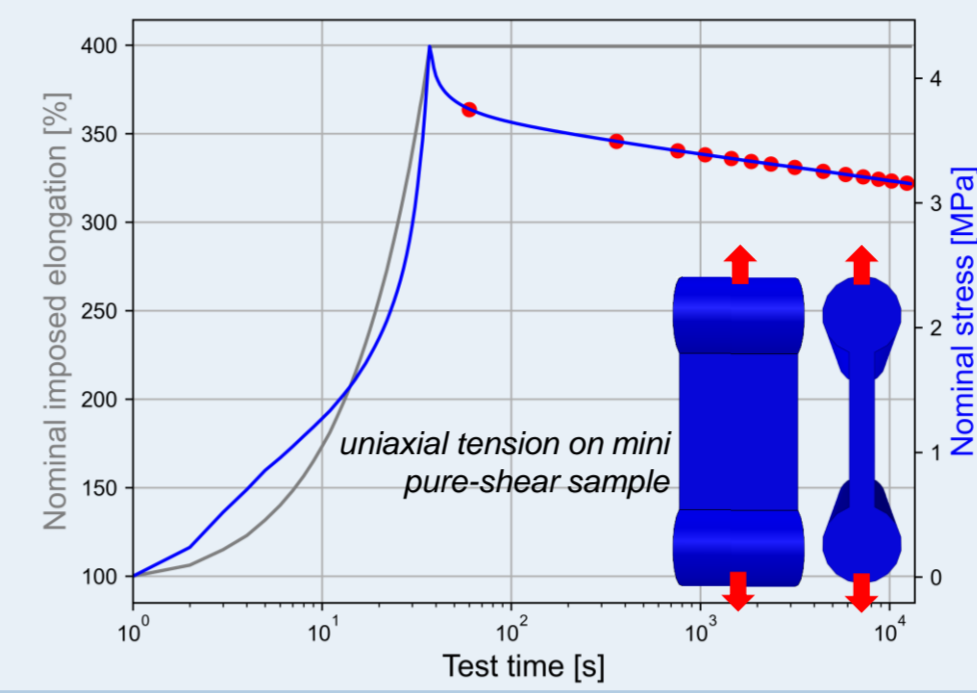
Material

Filled & cross-linked rubber :

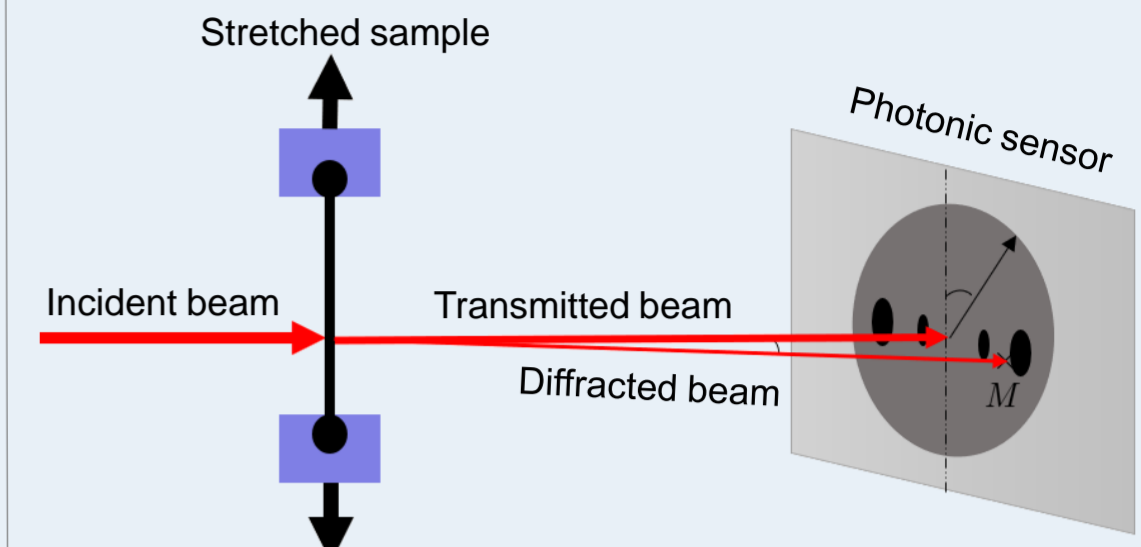
- Matrix : cis-polyisoprene
- Fillers : carbon black
- Vulcanizing agent : sulfur
- Other : processing agents, accelerators, plasticizers, antiozonants, ...

Performed Tests

- WAXD measures during stress relaxation for different temperatures and elongations



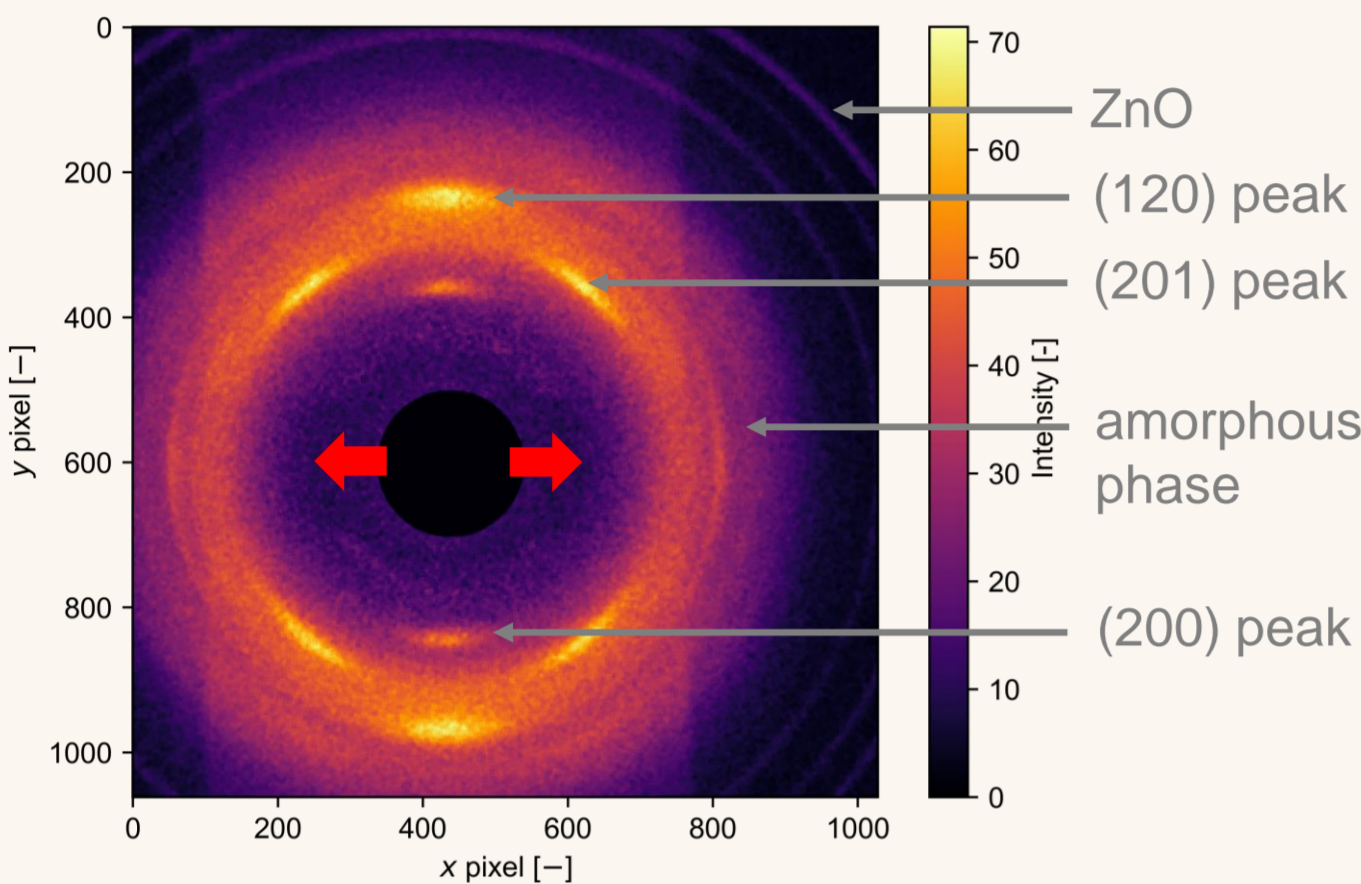
- Experimental setup :



- Tests performed at INSA Lyon with $\lambda = 1,54 \text{ \AA}$ and an exposure time of 240s

1 Raw data

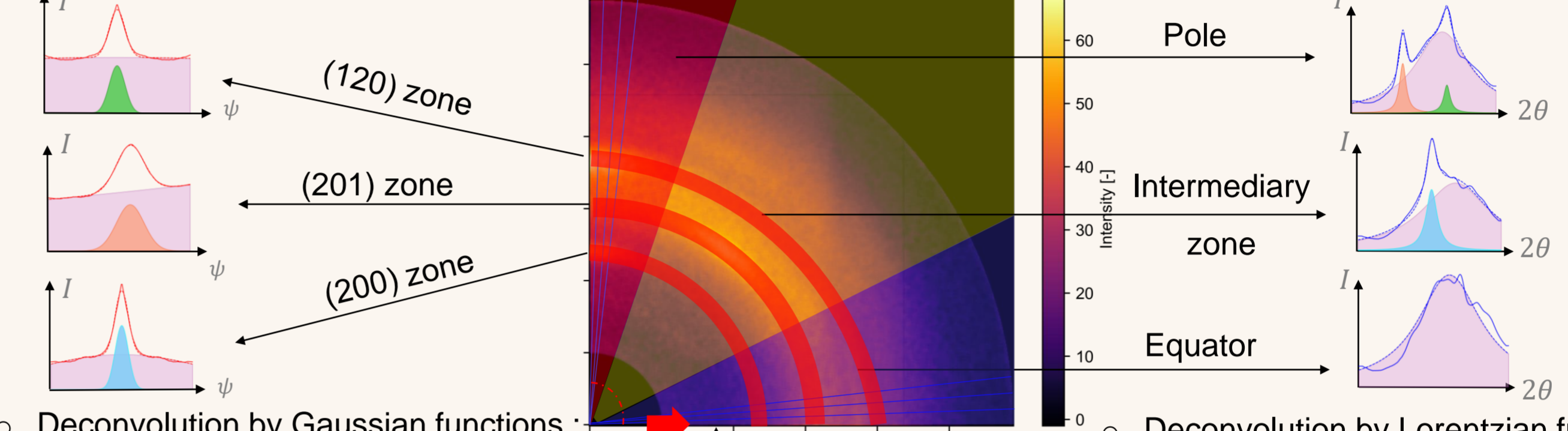
- Identification of (d_{hkl}) peaks and all other classic peaks from literature [1,2]



→ : tension direction

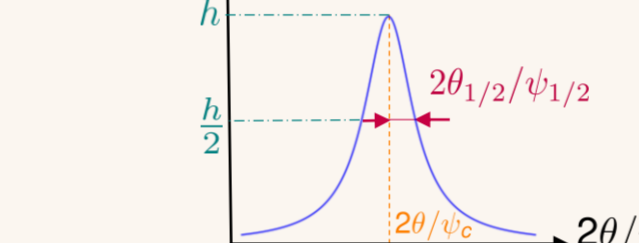
2 Profiles & Deconvolutions

- Use of **double symmetry [3]** to average the fourth quarters in one : noise reduction
- Definition of **2 types of profiles and deconvolution** by mathematical functions



- Deconvolution by Gaussian functions :

$$g(\psi, [h, \psi_c, \psi_{1/2}]) = h \exp\left(-\left(\frac{\psi - \psi_c}{\frac{\psi_{1/2}}{2\sqrt{\ln(2)}}}\right)^2\right)$$



$$L(2\theta, [h, 2\theta_c, 2\theta_{1/2}]) = \frac{h}{1 + \left(\frac{2\theta - 2\theta_c}{\frac{2\theta_{1/2}}{2}}\right)^2}$$

3 Lattice parameters

- Hypothesis of **orthorhombic lattice** for natural rubber
- Calculation of lattice parameters :

- $\lambda = 1,54 \text{ \AA}$
- $2\theta_{hkl}$: Bragg's angle at center of the (hkl) peak

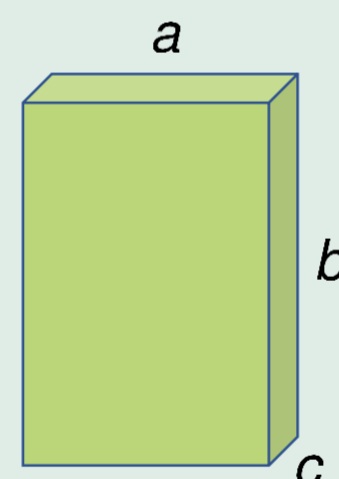
- Bragg's formula :

$$2d_{hkl} \sin(\theta_{hkl}) = n\lambda, \quad n \in \mathbb{N}^*$$

- Interreticular distance d_{hkl} for orthorhombic lattice :

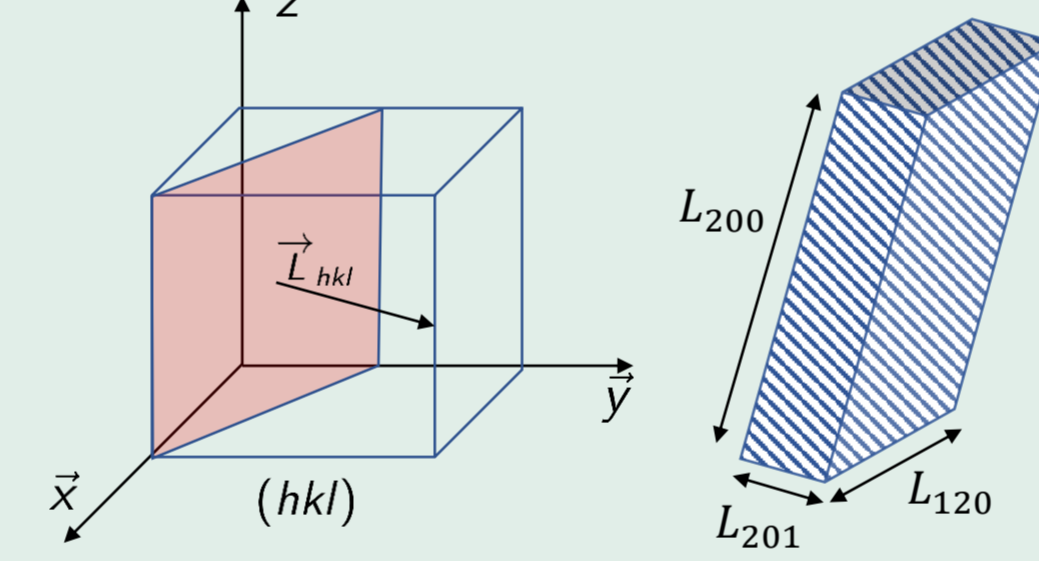
$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

	Beurrot, 2012 [3]	Poompradub, 2005 [4]	Here study
a [Å]	12,9	12,7	13,0
b [Å]	9,3	9,1	9,4
c [Å]	8,6	8,3	8,5



4 Crystallites size

- Three characteristic lengths : L_{200}, L_{201} & L_{120}

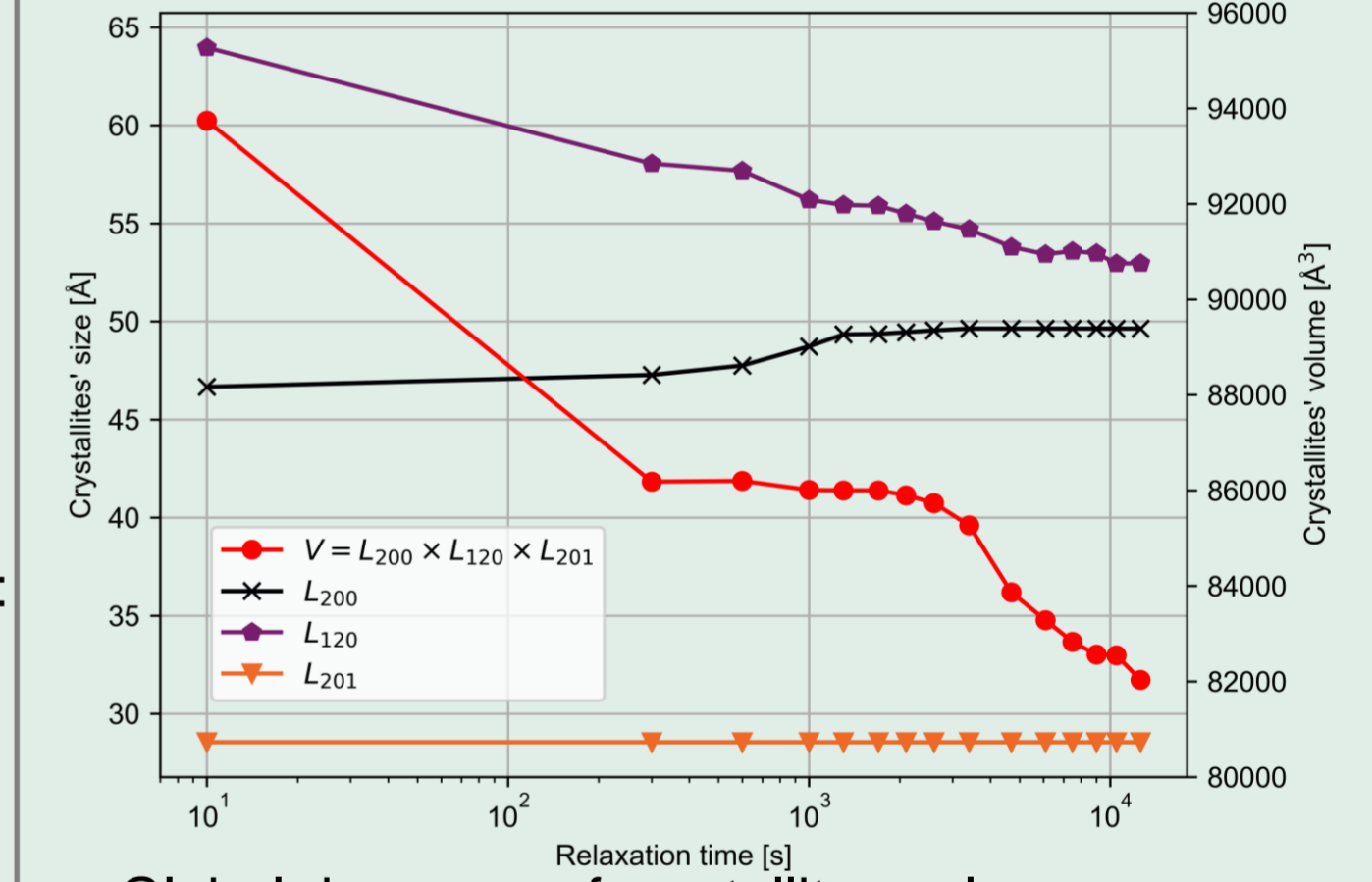


- Size calculated by **Debye-Scherrer formula** :

$$L_{hkl} = \frac{\lambda}{2\theta_{1/2, hkl} \cos(\theta_{hkl})}$$

- $\lambda = 1,54 \text{ \AA}$
- θ_{hkl} : half Bragg's angle at center of the (hkl) peak
- $2\theta_{1/2, hkl}$: FWHM of the Lorentzian function

- L_{hkl} represents the size of crystallites in the direction orthogonal to the (hkl) plane

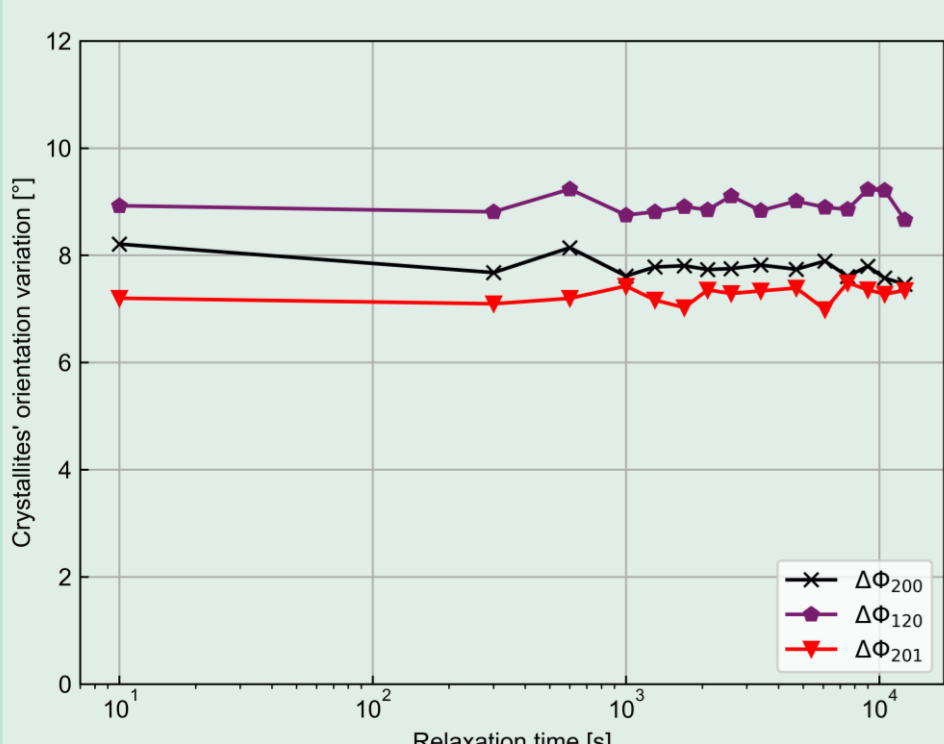
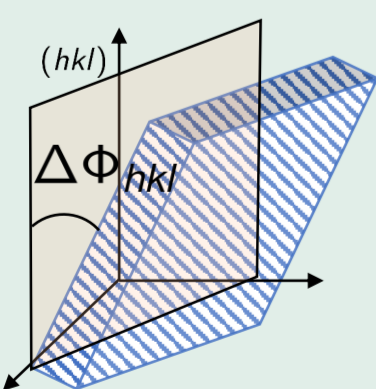


- Global decrease of crystallites volumes

5 Crystallites orientation

- Crystallites orientation variations $\Delta\Phi_{hkl}$ are given by full width at half maximum (FWHM) of the Gaussian function :

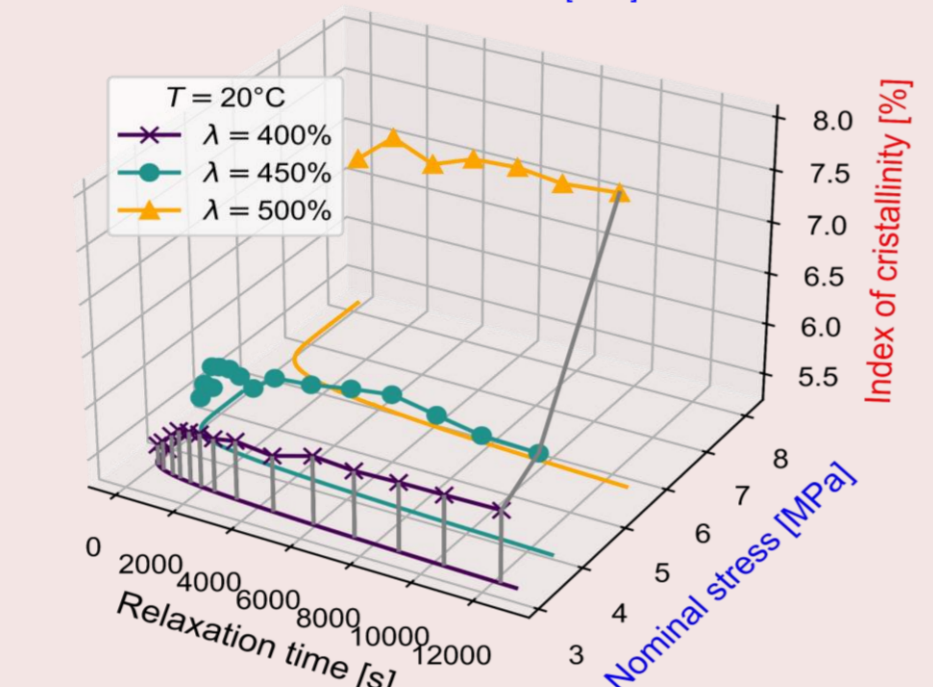
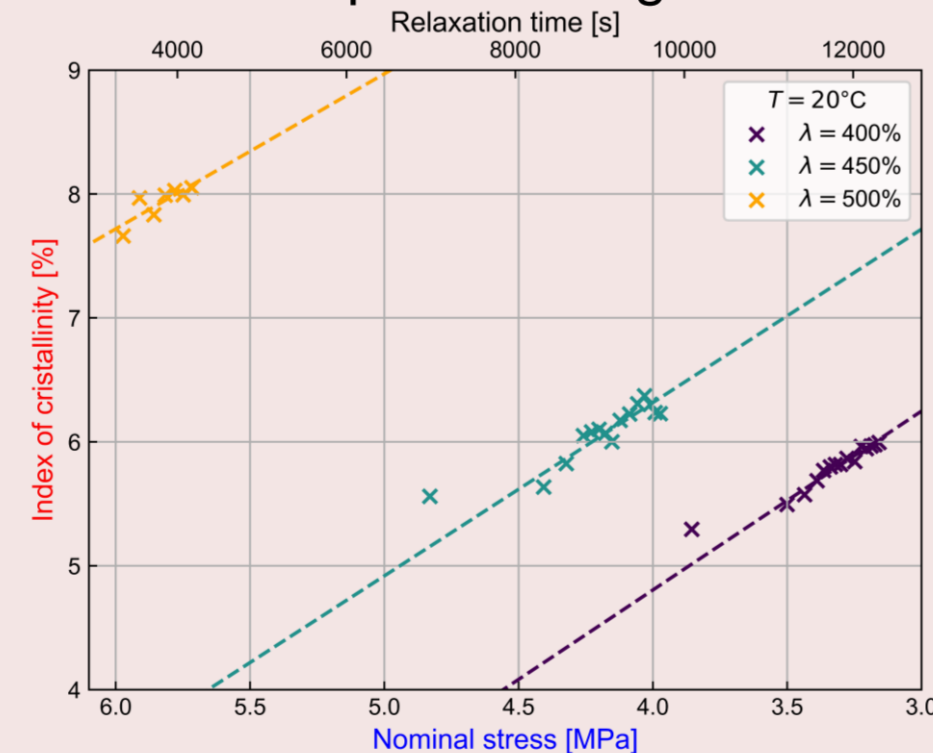
$$\Delta\Phi_{hkl} = \psi_{1/2, hkl}$$



- No variation of crystallites orientation during stress relaxation

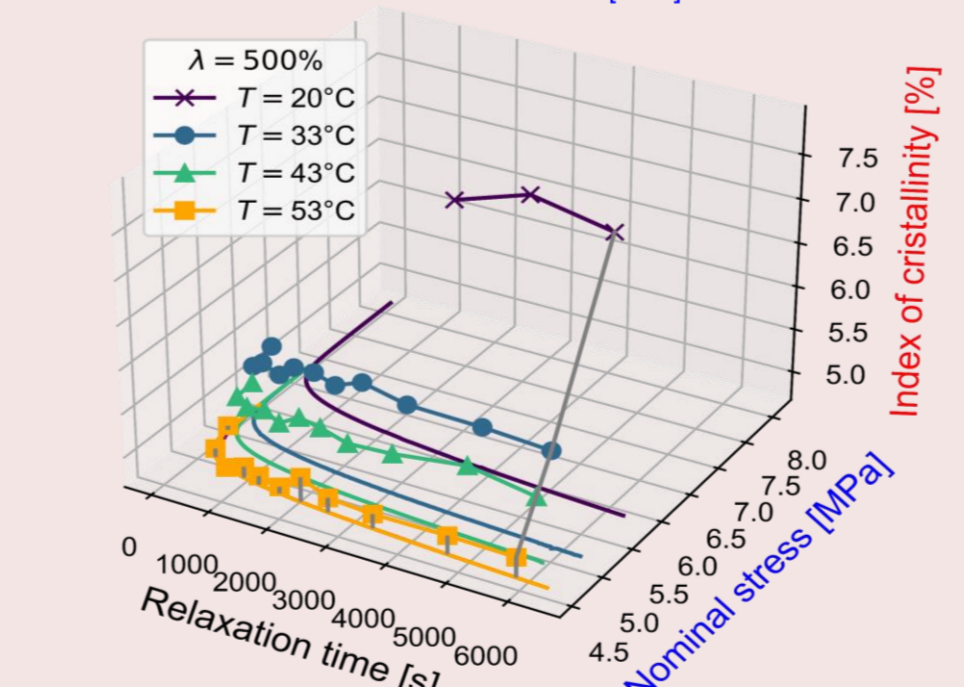
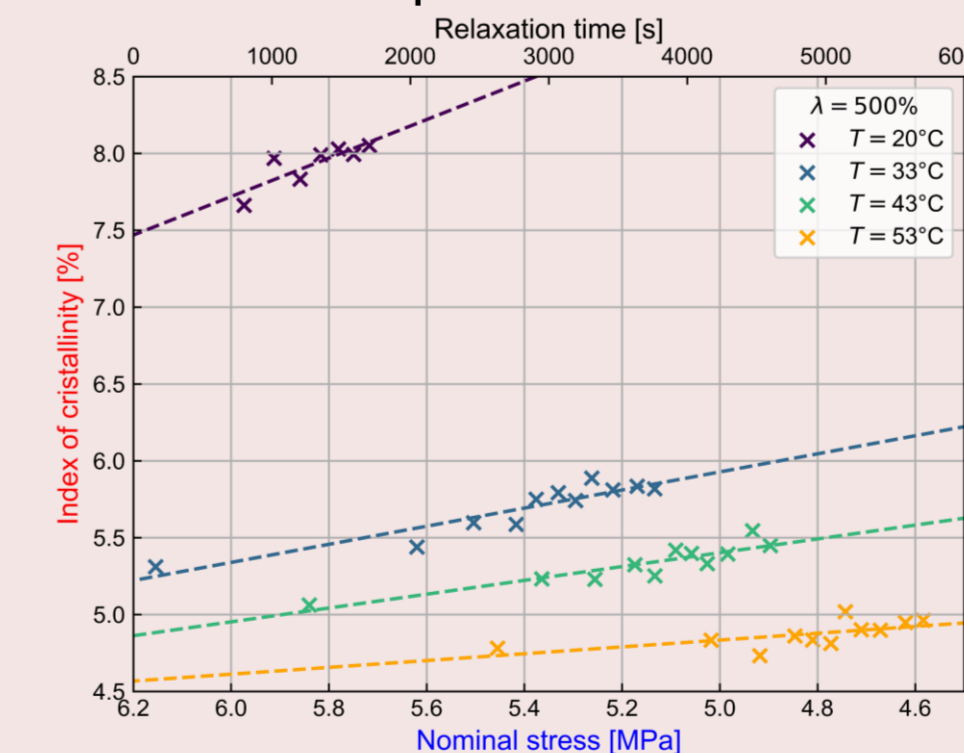
6 Crystallinity

- Effect of imposed elongation :



- During **stress relaxation**, the **index of crystallinity χ** varies linearly with **nominal stress σ** . The $\frac{\partial\chi}{\partial\sigma}$ coefficient remains the same whatever the value of the imposed elongation.

- Effect of temperature :



- During **stress relaxation**, temperature has two effects : it leads to lower **indexes of crystallinity χ** and it reduces the $\frac{\partial\chi}{\partial\sigma}$ coefficient (i.e. mechanically induced crystallization kinetics).

Conclusion & Perspectives

There are first results for this study. During stress relaxation :

- The crystallinity index increases while the volume of crystallites decreases. It is probably due to a **fragmentation** of crystallites.
- The coefficient $\frac{\partial\chi}{\partial\sigma}$ remains constant i.e. the **crystallinity index evolves linearly with stress**. This coefficient also decreases with temperature. Next steps of this study are *in-situ* WAXD measures on more complex sollicitations : **relaxing and non-relaxing cyclic tests**.

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