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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



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.

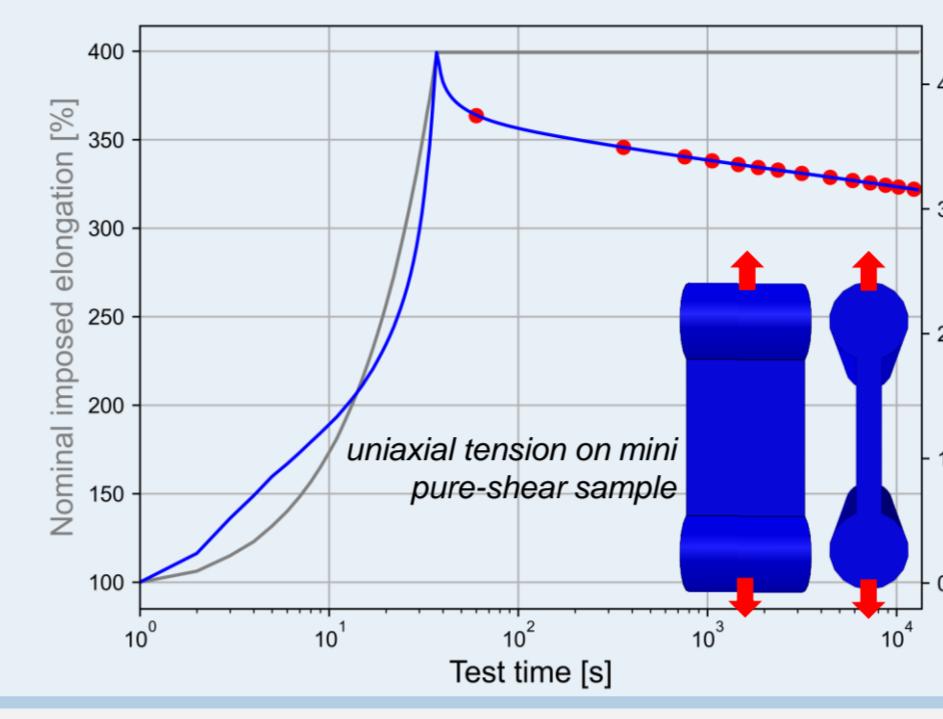
## Material

### Filled & cross-linked rubber :

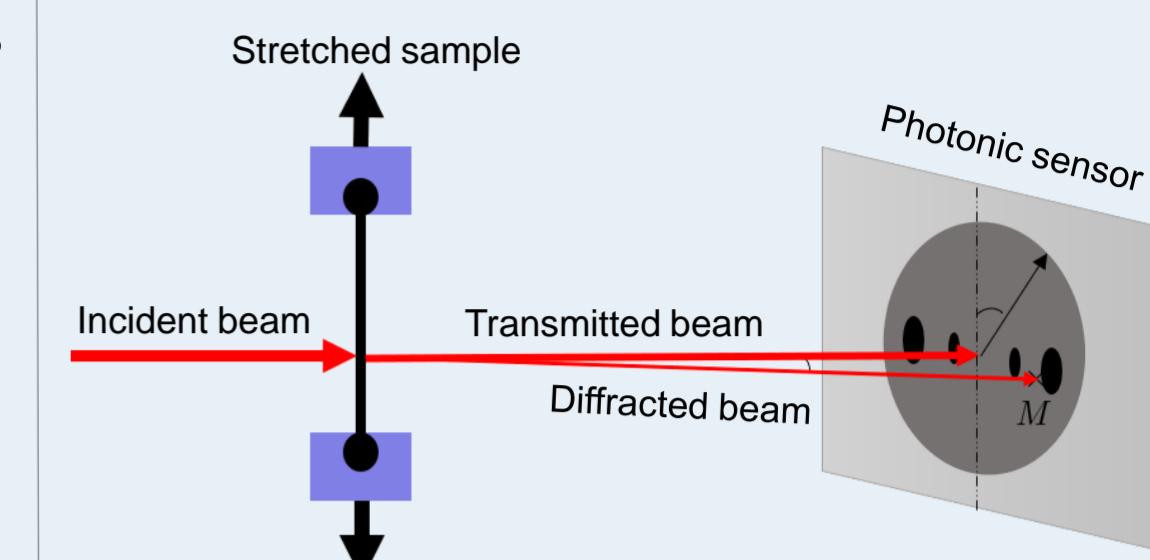
- Matrix : cis-polyisoprene
- Fillers : carbon black
- Vulcanizing agent : sulfur
- Other : processing agents, accelerators, activators, plasticizers, antiozonants, ...

## Performed Tests

- WAXD measures** during stress relaxation for different temperatures and elongations



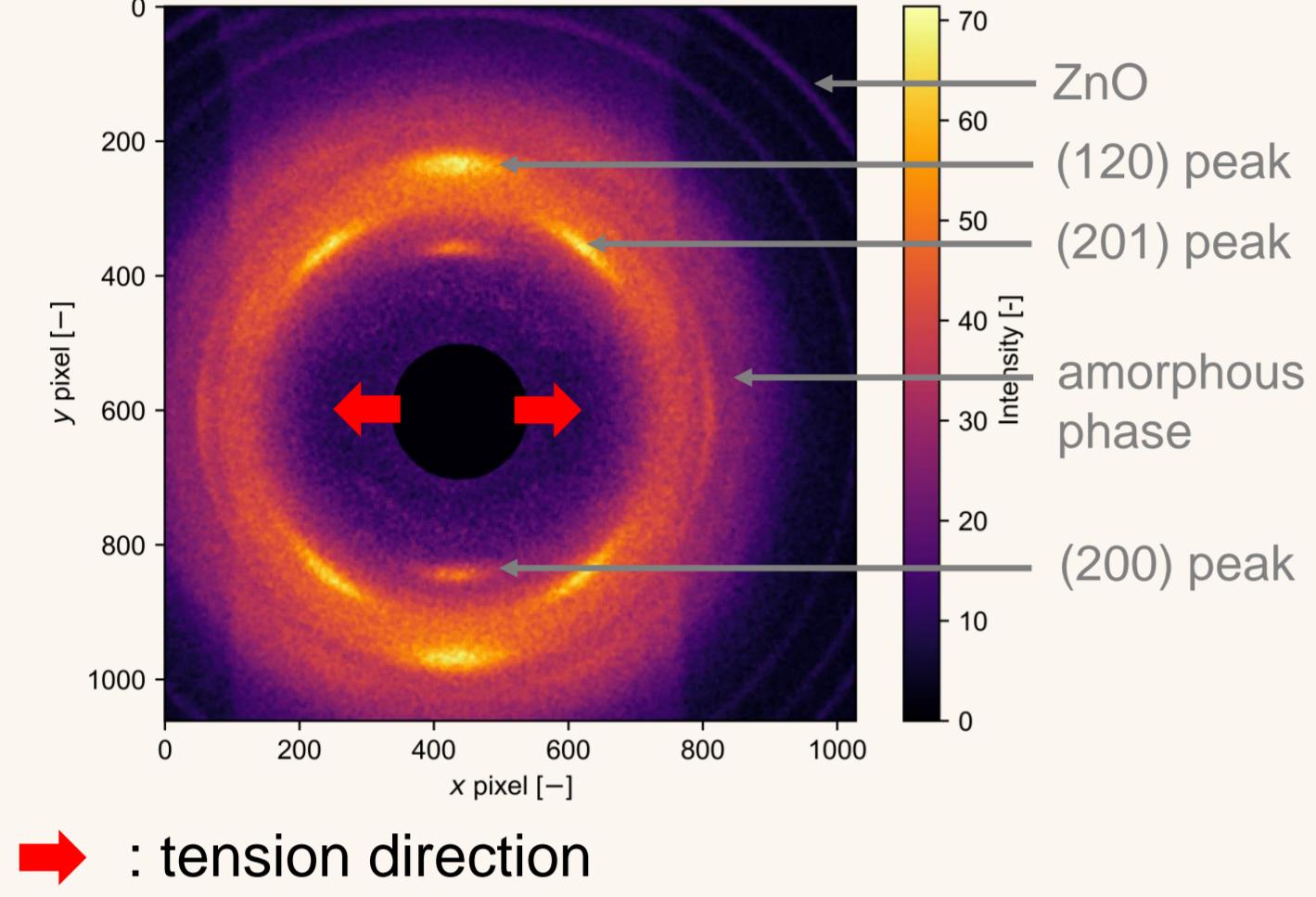
- Experimental setup :



- Tests performed at INSA Lyon with λ = 1.54 Å and an exposure time of 240s

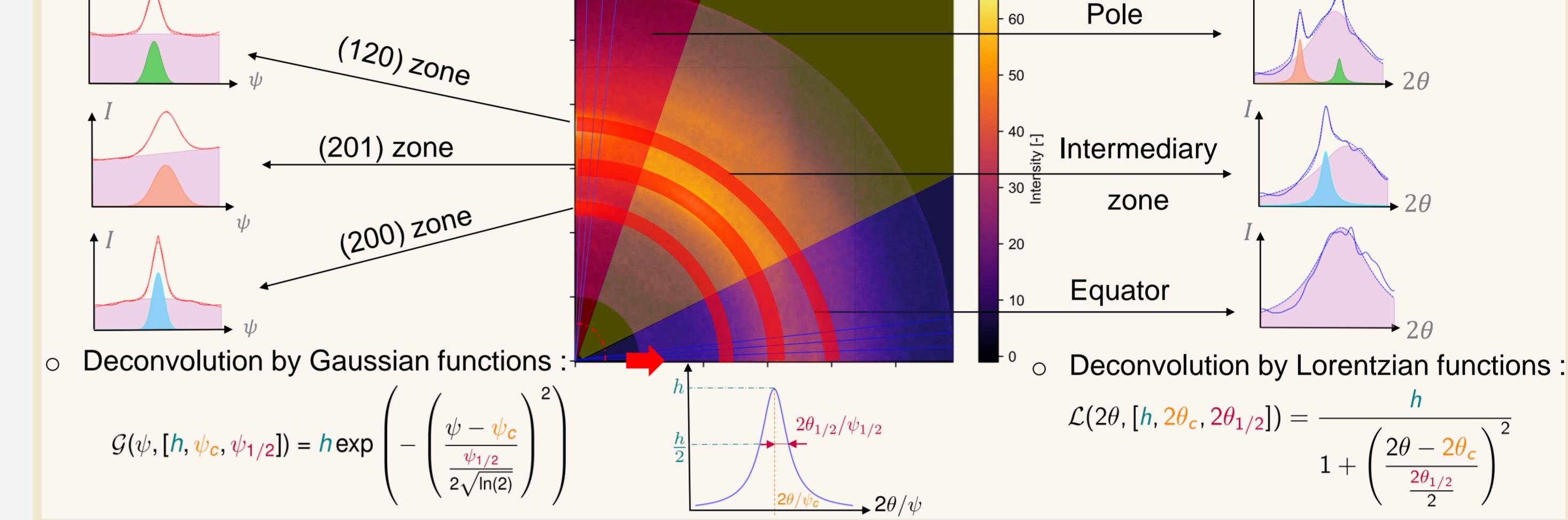
## 1 Raw data

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



## 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

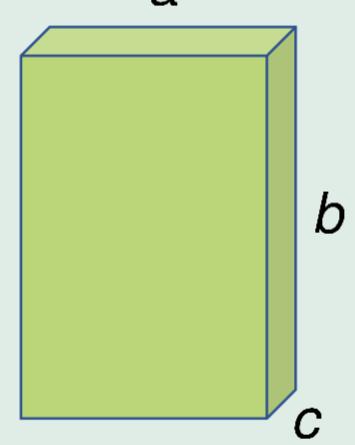


## 3 Lattice parameters

- Hypothesis of **orthorhombic lattice** for natural rubber
- Calculation of lattice parameters :
  - Bragg's formula :  $2d_{hkl} \sin(\theta_{hkl}) = n\lambda$ ,  $n \in \mathbb{N}^*$
  - Interreticular distance  $d_{hkl}$  for orthorhombic lattice :

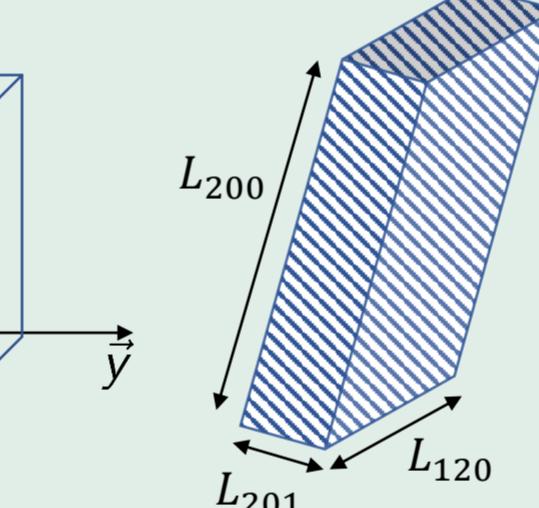
$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

	Beurrot, 2012 [3]	Poompradub, 2005 [4]	Here study
$a [\text{\AA}]$	12,9	12,7	13,0
$b [\text{\AA}]$	9,3	9,1	9,4
$c [\text{\AA}]$	8,6	8,3	8,5



## 4 Crystallites size

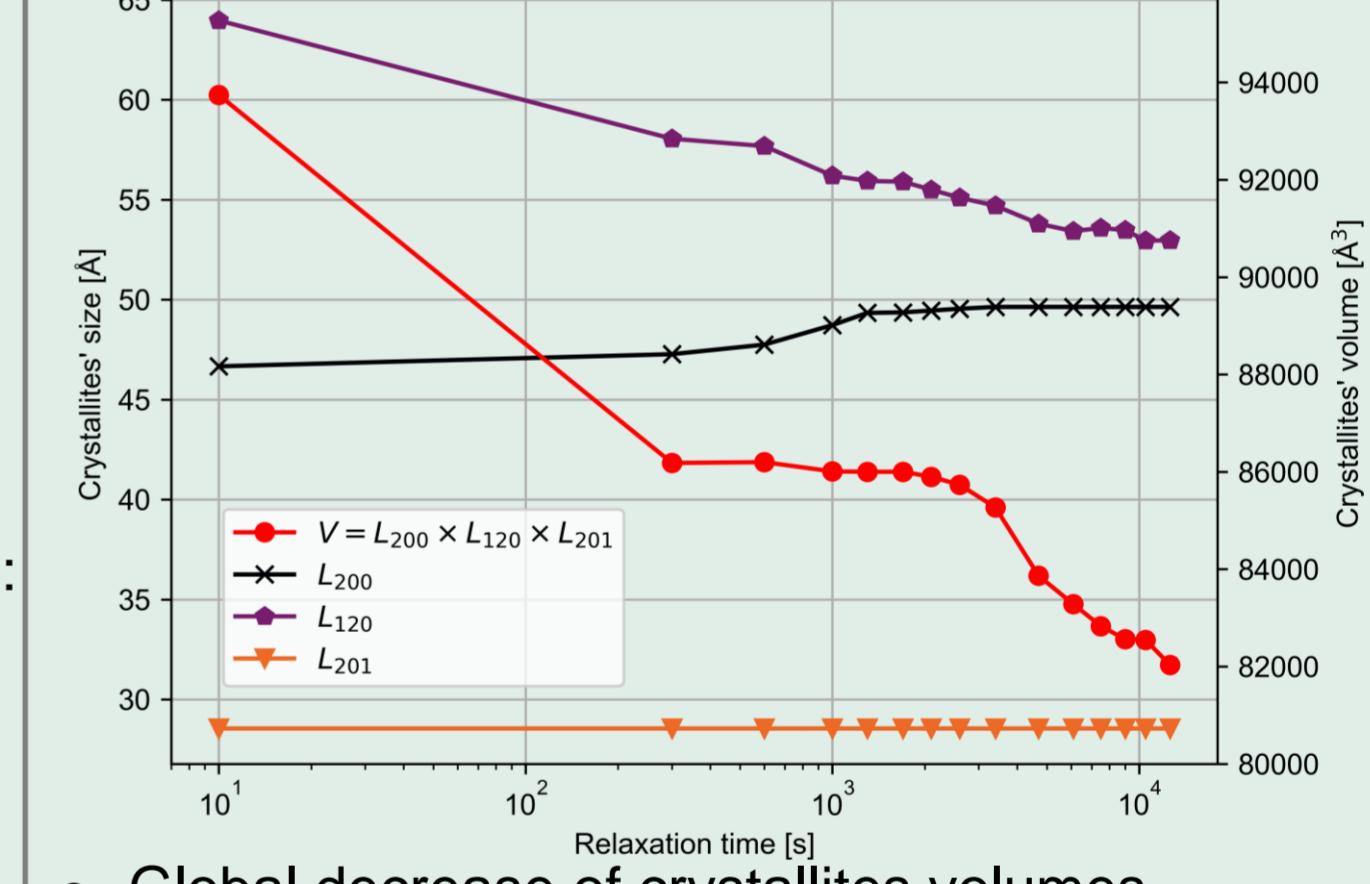
- Three characteristic lengths :  $L_{200}$ ,  $L_{201}$  &  $L_{120}$



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

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

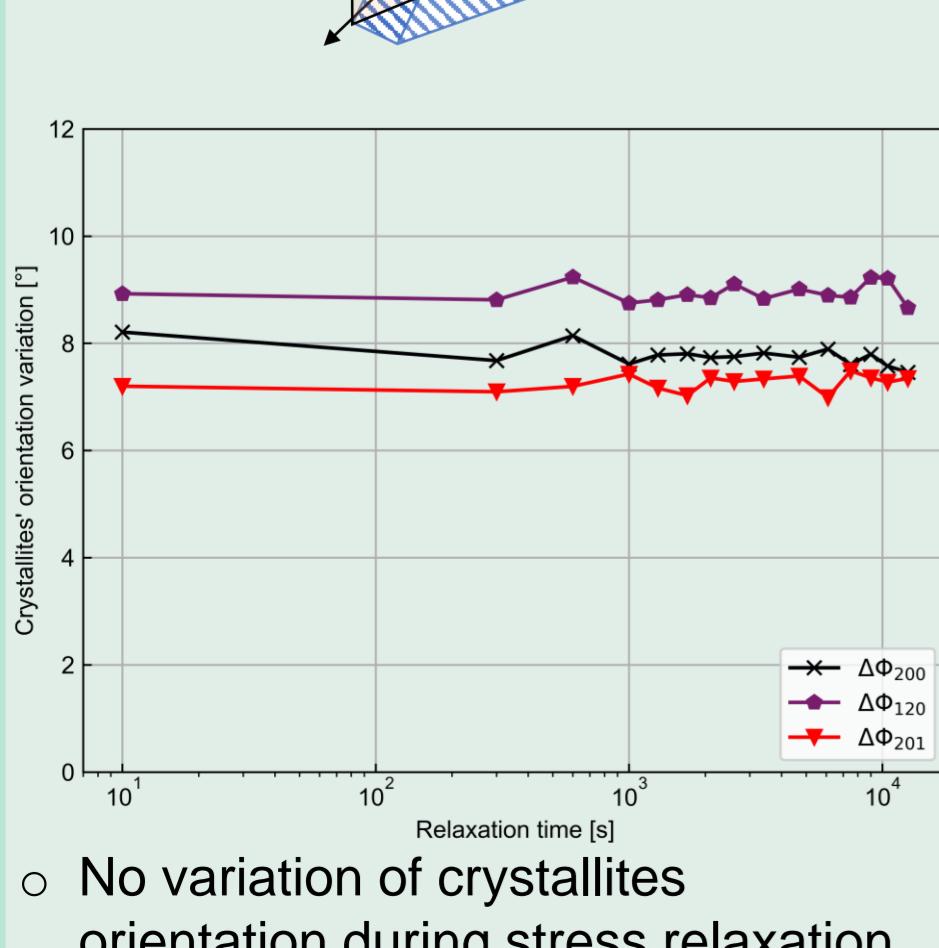
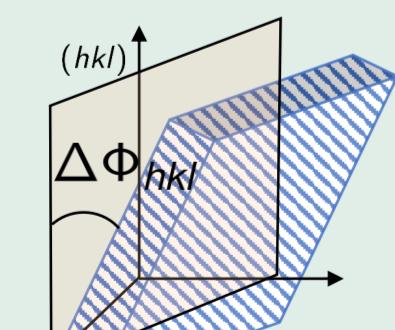
- $L_{hkl}$  represents the size of crystallites in the direction orthogonal to the  $(hkl)$  plane



## 5 Crystallites orientation

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

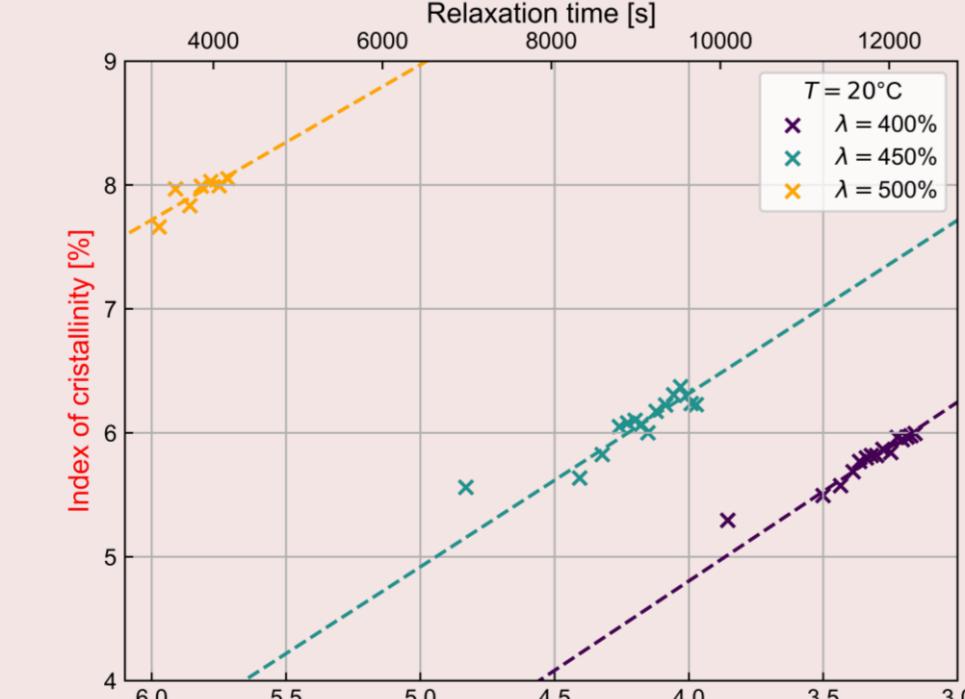
$$\Delta\Phi_{hkl} = \psi_{1/2,hkl}$$



- No variation of crystallites orientation during stress relaxation

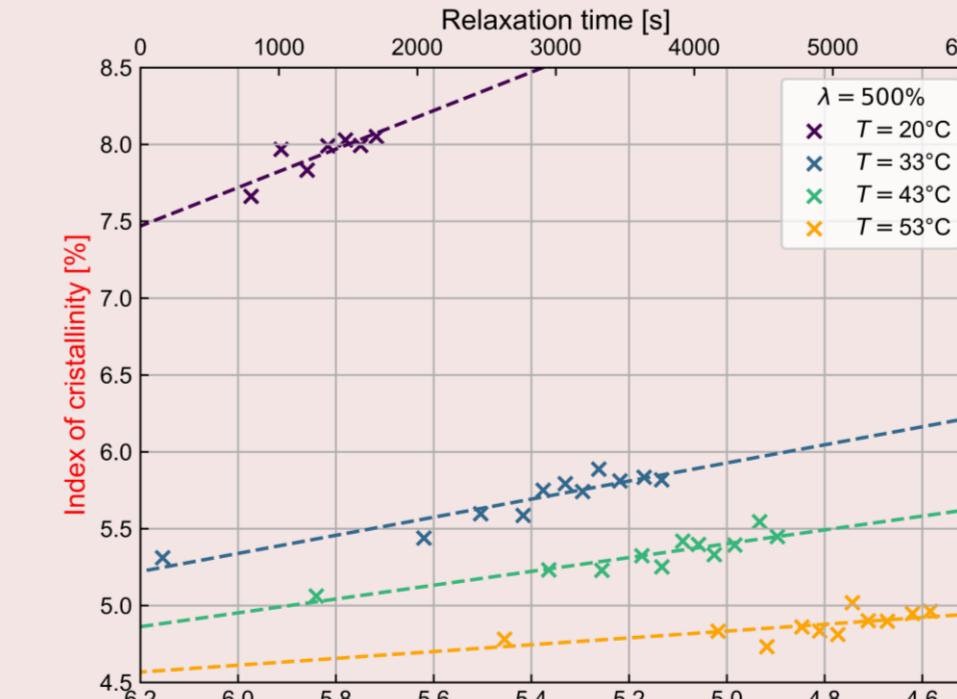
## 6 Cristallinity

- Effect of imposed elongation :



- During stress relaxation, the index of crystallinity  $\chi$  varies linearly with nominal stress  $\sigma$ . 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  $\chi$  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  $\frac{d\chi}{d\sigma}$  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 solicitations : **relaxing and non-relaxing cyclic tests**.

## References

- [1] N. Candau, « Compréhension des mécanismes de cristallisation sous tension des élastomères en conditions quasi-statiques et dynamiques », Thesis, INSA Lyon, 2014
- [2] P.-A. Albouy, J. Marchal, et J. Rault, « Chain orientation in natural rubber, Part I: The inverse yielding effect », Eur. Phys. J. E, vol. 17, n° 3, p. 247-259, 2005.
- [3] S. Beurrot, « Cristallisation sous contrainte du caoutchouc naturel en fatigue et sous sollicitation multiaxiale », Thesis, Ecole Centrale de Nantes, 2012
- [4] S. Poompradub et al., « Mechanism of strain-induced crystallization in filled and unfilled natural rubber vulcanizates », Journal of Applied Physics, vol. 97, 2005.

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